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Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

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REACTION OF GLASSY SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

8. ACTION OF ACID SOLUTIONS ON GLASSY SODIUM ALUMINOSILICATES WITH VARIABLE ACID NUMBER

S. K. Dubrovo

The problem of the bonding of silicon and aluminum in silicates is one of the most important problems of the chemistry of silicates. Only thorough investigation of the chemical and the physical properties of both the natural and the artificial crystalline and glassy aluminosilicates will be able to clarify properly the role of aluminum in the silicates.

As is known, aluminum exists in natural silicates in coordination number of four or six relative to the oxygen atoms, being in the first case a structural analog of silicon, in the second case – of magnesium [1]. It is interesting, from this viewpoint, to study the reaction of aqueous solutions on the aluminosilicates, especially that of acidic solutions. Geochemists and crystallochemists have been using widely the determination of acid-resistance of silicate minerals for the purpose of their classification [2]. Contradictory data have been expressed in the literature concerning the effect of alteration of coordination of aluminum on the acid-resistance of the silicates. While Sobolev considers that aluminum with coordination of four is the weak link in the silicate structure [3], Brindley and Youell [4] come to the conclusion that aluminum with coordination number of four is more firmly retained in the structure, as shown by their experiments on the reaction of acid solutions on chlorites. As it was shown by our studies of the glassy sodium aluminosilicates, the acid-resistance depends mainly on the proportion of silica and aluminum oxide in these simple three-component glasses, even in cases in which the aluminum coordination is evidently unchanged [5, 6]. The same followed from some experiments performed by Lyle, Horak and Scharp [7], who determined the chemical stability of calcium-sodium-aluminosilicate glasses relative to 0.05 N solution of hydrochloric acid.

Previously we studied the reaction of solutions of acids on glassy aluminosilicates which corresponded to sodium bisilicate in composition with additions of 0.05 to 1 mole of aluminum oxide [5, 6]. The course of chemical destruction of these glasses was regarded by us in its relation to the degree of depolymerization of silica in the aluminosilico-oxygen skeleton of the glass, i.e., in its dependence on the rupture of Si-O-Si bonds. The action of the acids consisted of selective leaching of sodium and aluminum ions with formation of a residual silica layer on the glass surface. With increase of the content of aluminum oxide in the original glass, the number of isolated, unconnected silicon-oxygen groups which are capable of passing into solution in an alkali treatment increased accordingly. The goal of the present study was the examination of the action of alteration of silica and alumina proportion in sodium-aluminosilicate glasses on their acid resistance, the glasses being richer in silica than those studied previously.

The degree of bonding or polymerization of the skeleton of the silicate glass has been characterized by many workers by means of the oxygen number [8]; this number is equal to the ratio of the number of gram-atoms of oxygen to the number of gram-atoms of silicon,in case of simple silicates,or to the sum of silicon and aluminum in case of aluminosilicates. With increased content of the alkali and alkaline earth oxides in the composition of simple silicate glasses, the degree of polymerization of silica in the glass carcass decreases, which fact is accompanied by the increasing oxygen number. The oxygen number changes from two to three after the

change of the glass composition from purely siliceous to the corresponding metasilicate. The same rule applies to the aluminosilicate glasses with maintenance of constant ratio of aluminum and silicon. With the same molar content of alkali oxide in aluminosilicate glasses, the oxygen number characterizes the proportion of aluminum and silicon in the glass carcass. Reduction of the relative content of aluminum is accompanied in this case by increased oxygen number.

We studied the behavior of four series of glasses in the composition range: $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, $Na_2O \cdot Al_2O_3 \cdot 3SiO_2$, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, in solutions of acids, with maintenance in each series of the same molar content of sodium oxide and with alteration of the proportion of alumina and silica.

EXPERIMENTAL

The starting materials in each series were glasses of the type $Na_2O \cdot Al_2O_3 \cdot nSiO_2$, where n = 2, 3, 4 and 6 with oxygen number of two. The following members of a given series were prepared by successive replacement of part of aluminum oxide in the original glass by silica (in molar ratios),which change was accompanied by increase of the oxygen number. One of the glasses – No. 6 – was prepared by increasing the aluminum oxide content by 0.1 mole at the expense of silica in the glass,which in its composition corresponded to jadeite. The oxygen number in glasses studied by us varied from 1.98 to 2.12. Chemically pure materials were used for the fusion. Fusion of most of the glasses was done in one-and three-liter quartz crucibles in a flame-heated oven. In case of a considerable deviation of the composition of the glass from the synthetic formula and the analytical data, the fusion was repeated in a platinum crucible in a furnace with silit rods. As we had established previously, a close agreement of glass compositions from synthetic and analytical data is always observed in fusion of the glass in a platinum crucible. All glasses, except No. 8 and 9 which were repeatedly fused in a platinum crucible, were analyzed and their compositions are shown in Table 1.

TABLE 1

Composition of the Examined Sodium Aluminosilicates, in Mole Percent

No. of glass	According to synthesis			According to analysis		
	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2
1	12,50	12,50	75,0	13,20	12,10	74,50
2	12,50	8,75	78,75	13,00	8,55	78,55
3	16,66	16,66	66,70	17,00	16,30	66,70
4	16,66	12,48	70,86	16,70	11,60	71,70
5	16,66	8,34	75,00	15,50	8,25	76,25
6	16,66	18,34	65,00	16,70	18,40	65,00
7	Molten nephelin			23,80	24,60	51,60
8	25,00	21,30	53,70	($Na_2O + K_2O$)	—	—
9	25,00	16,25	58,75	—	—	—
10	20,00	20,00	60,00	19,70	19,10	61,20
11	20,00	16,00	64,00	20,40	16,20	63,40
12	20,00	10,00	70,00	20,60	9,35	70,05
13	30,30	9,10	60,60	30,30	9,10	60,60

Glasses No. 1 and 2 belong, by their chemical composition, to the series of feldspar, those of No. 3-6 – to glasses of jadeite type; glass No. 7 is glassy nephelin prepared by fusion of natural nephelin; glasses No. 8 and 9 are commercial glasses of the nephelin series, while No. 10-12 are intermediate between the nephelin and the jadeite type glasses.

The chemical stability of these glasses was determined in respect to 0.1 N and N hydrochloric acid solutions at the temperature of 40° in a quartz apparatus. Determinations were made of all components which passed into solution from the glass after 1, 2, 4 and 6 hours, with colorimetric methods previously used by us [5]. Powder of the glasses, passed through sieves with hole diameters of 0.105-0.149 mm, then washed free of the dust fraction with alcohol, and dried at 110°, was used for the experiments. Earlier, we used glass plates for the

TABLE 2

Reaction of Sodium Aluminosilicates with Hydrochloric Acid Solutions at 40°

No. of the glass	Molar ratio (by analysis)			Oxygen number	Acid concentration in N	n in moles/cm²·10^6, β, α	Time, in hours			
	Na_2O	Al_2O_3	SiO_2				1	2	4	6
1	1	0,92	5,64	2,00	0,1	n_{Na_2O}	—	—	—	0,01
						$n_{Al_2O_3}$	—	—	—	0,01
						n_{SiO_2}	—	—	—	0,004
2	1	0,70	6,30	2,05	0,1	n_{Na_2O}	—	0,02	0,02	0,04
						$n_{Al_2O_3}$	—	0,01	0,01	0,01
						n_{SiO_2}	—	0,04	0,04	0,04
3	1	0,96	3,92	2,0	0,1	n_{Na_2O}	0,39	0,71	0,80	0,86
						$n_{Al_2O_3}$	0,37	0,61	0,71	0,64
						n_{SiO_2}	0,12	0,18	0,24	0,27
						β	0,99	0,90	0,92	0,80
						α	0,08	0,06	0,08	0,08
3	1	0,96	3,92	2,0		n_{Na_2O}	2,2	3,2	7,6	9,2
						$n_{Al_2O_3}$	2,0	3,3	6,7	8,0
						n_{SiO_2}	0,6	1,8	1,9	2,0
						β	0,95	1,07	0,92	0,91
						α	0,07	0,15	0,07	0,06
4	1	0,69	4,29	2,05	0,1	n_{Na_2O}	0,03	—	—	0,05
						$n_{Al_2O_3}$	—	0,03	0,03	0,04
						n_{SiO_2}	0,007	0,014	0,015	0,017
5	1	0,483	4,82	2,08	0,1	n_{Na_2O}	0,05	—	0,07	0,07
						$n_{Al_2O_3}$	0,01	0,01	0,01	0,01
						n_{SiO_2}	—	0,02	0,02	0,02
5	1	0,483	4,82	2,08	1	n_{Na_2O}	—	—	—	0,03
						$n_{Al_2O_3}$	0,02	0,01	0,02	0,02
						n_{SiO_2}	0,09	0,08	0,08	0,07
6	1	1,1	3,9	1,98	0,1	n_{Na_2O}	1,65	2,87	5,20	6,88
						$n_{Al_2O_3}$	1,77	3,10	4,83	6,34
						n_{SiO_2}	1,39	2,78	5,0	5,80
						β	0,98	0,98	0,84	0,83
						α	0,25	0,25	0,25	0,23
8	1	0,85	2,15	2,04	0,1	n_{Na_2O}	5	7,5	8,6	9,5
						$n_{Al_2O_3}$	4,7	6,4	6,6	6,6
						n_{SiO_2}	12,5	17,0	18,3	16,7
						β	1,1	1,0	0,91	0,81
						α	1,04	1,1	0,99	0,82

TABLE 2 (continued)

No. of the glass	Molar ratio (by analysis) Na₂O			Oxygen number	Acid concentration in N	n in moles/cm²·10^6 β α	Time, in hours 1	2	4	5
	Na_2O	Al_2O_3	SiO_2				1	2	4	5
9	1	0,65	2,35	2,09	0,1	n_{Na_2O}	4	7,8	10,2	11,5
						$n_{Al_2O_3}$	2,9	5,1	5,8	6,1
						n_{SiO_2}	11,5	19,3	21	21
						β	1,1	1,01	0,88	0,82
						α	1,2	1,05	0,88	0,75
10	1	0,97	3,11	2,0	0,1	n_{Na_2O}	3,8	8,0	8,7	9,6
						$n_{Al_2O_3}$	3,3	5,6	6,5	7,0
						n_{SiO_2}	8,6	14,9	20	21
						β	0,90	0,72	0,78	0,76
						α	0,73	0,61	0,74	0,70
11	1	0,80	3,10	2,04	0,1	n_{Na_2O}	2,5	4,5	7,9	9,0
						$n_{Al_2O_3}$	1,8	3,4	5,1	5,6
						n_{SiO_2}	1,2	2,1	3,2	3,4
						β	0,90	0,95	0,80	0,78
						α	0,16	0,15	0,13	0,12
12	1	0,45	3,40	2,12	0,1	n_{Na_2O}	0,02	0,04	0,06	0,07
						$n_{Al_2O_3}$	0,07	0,01	0,01	0,01
						n_{SiO_2}	0,02	0,02	0,03	0,03
13	1	0,3	2	2,27	0,1	n_{Na_2O}	0,69	0,88	1,07	1,20
						$n_{Al_2O_3}$	0,09	0,14	0,19	0,20
						n_{SiO_2}	0,07	0,09	0,11	0,13
						β	0.43	0,53	0,59	0,55
						α	0,05	0,05	0,05	0,05

specimens. The use of the powder method was caused by the relatively greater chemical resistance of the majority of glass-like aluminosilicates and the need, because of this, to use samples with the largest possible surface. Usually 120 ml of the acid and 1 g of the powder were used, this amount being approximately correspondent to the summary surface of about 200 cm².

As shown by specially set-up experiments, the alteration of the ratio of the powder surface to the volume of the solution used affects the rate of leaching rather slightly. The amounts of components which pass into solution, for the unstable glasses, depend greatly on the ratio of the surface of the sample under test to the volume of the solution used. In this case, both the concentration of the components passed into the solution from the glass and the concentration of the acting acid are materially changed with time upon an increase of the surface with the same volume being maintained. This may retard the rate of the leaching process. From these considerations, in running experiments with the unstable glasses of the nephelin type (No. 9), we ran some additional experiments with 0.05 g of the powder in the same volume of the acid. For purposes of comparison, we also determined, by the powder method, the chemical resistance of glass with composition $Na_2O \cdot 0.3Al_2O_3 \cdot$ $\cdot 2SiO_2$ (No. 13), studied previously in the form of specimens as plates. The amounts of Na_2O, Al_2O_3 and SiO_2, determined in the solution, were recalculated to the number of moles of the corresponding oxides and were related to 1 sq cm of the surface. These values are shown in the tables in the form n_{Na_2O}, $n_{Al_2O_3}$ and n_{SiO_2}. For characterization of the process, we also used the values of: $\alpha = \frac{n_{SiO_2}}{mn_{Na_2O}}$ and $\beta = \frac{n_{Al_2O_3}}{kn_{Na_2O}}$, which express, respectively, the fraction of silica and alumina which had passed into solution from the glass layer which had

TABLE 3

Reaction of Glassy Sodium Aluminosilicates of Nephelin Type with 0.1 N Solution of Hydrochloric acid at 40°
(sample of 0.5 g)

No. of the glass	Na_2O	Molar ratio (by analysis)		Oxygen number	n in moles/cm²·10^6, β, α	Time, in hours			
		Al_2O_3	SiO_2			1	2	4	6
7	1	1,03	2,16	1,99	n_{Na_2O}	13,3	15,7	17,1	17,8
					$n_{Al_2O_3}$	13,0	15,1	15,4	16,5
					n_{SiO_2}	32,0	37,5	35,0	39,0
					β	0,95	0,97	0,90	0,93
					α	1,10	1,10	0.95	1,0
8	1	0,85	2,15	2,04	n_{Na_2O}	4,5	8,7	13,9	17,8
					$n_{Al_2O_3}$	3,1	7,8	11,3	12,9
					n_{SiO_2}	—	19,2	32,9	36,6
					β	0,95	1,1	1,1	0,86
					α	—	1,02	1,08	0,96
9	1	0,65	2,35	2,09	n_{Na_2O}	5,5	10,5	16,6	20,8
					$n_{Al_2O_3}$	3,6	6,7	9,5	10,5
					n_{SiO_2}	—	34,3	38	43
					β	1	0,98	0,90	0,80
					α	—	1,3	0,98	0,90

reacted with the solution. The values of m and k represent the number of moles of silica and alumina in the original glass whose composition is expressed in the form $Na_2O \cdot kAl_2O_3 \cdot mSiO_2$. The results are given in Tables 2 and 3.

Data in Table 2 indicate that feldspar type glasses belong to the highly resistant glasses, whose behavior in hydrochloric acid solution is practically unchanged with alteration of the oxygen number. The chemical resistance of glasses of the jadeite type rises with increase of oxygen number from 1.98 to 2.05, the passage of all components into solution being thus decreased. Thus, from 1 : 1.1 : 3.9 glass, with oxygen number 1.98, 115 times more Na_2O passes into solution in 6 hours than from the 1 : 0.69 : 4.29 glass with oxygen number 2.05. Correspondingly, the values of $\frac{n_{Al_2O_3}}{k}$ and $\frac{n_{SiO_2}}{m}$ for 6 hours are 95 and 37 times greater for the first glass. With further increase of the oxygen number in this series, from 2.05 to 2.08, the chemical resistance of the glasses remains practically unchanged.

The process of the reaction of all these glasses with 0.1 N hydrochloric acid solution proceeds so that sodium oxide and aluminum oxide pass into solution in practically the same proportions as those in which they were present in the original glass (value of β is near unity); the silicic acid however passes into solution in considerably smaller amounts. Owing to this, a residual layer is formed on the surface which is enriched by silica: the fraction of silica which had passed into solution does not exceed 25% (α = 0.05–0.25). The same character of destruction is maintained also in the action of N hydrochloric acid, although the rate of passage of all components into solution from the glass increases for the less resistant glasses and is not changed for the highly resistant ones (glasses No. 3 and 5).

In the series of glasses with 1 : 1 : 3 composition (No. 10-12) the chemical resistance also rises with increased oxygen number from 2.0 to 2.12. With change of oxygen number from 2.0 to 2.04 the passage of silicic acid into solution from these glasses decreases by 5-7 fold over the various time intervals, while the passage of other components – sodium oxide, aluminum oxide – into solution is practically unchanged. A further increase of the oxygen number from 2.04 to 2.12 in this series leads to a sharp decrease of passage of all components into solution. For glasses of this type the predominant leaching of sodium and aluminum ions is also characteristic,

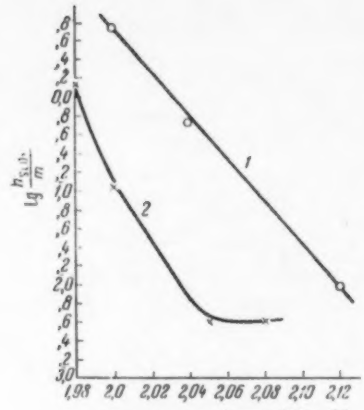

Fig. 1. Dependence of the amount of silica passed into solution on the oxygen number:
1) glasses of type 1 : 1 : 3; 2) glasses of type 1 : 1 : 4.

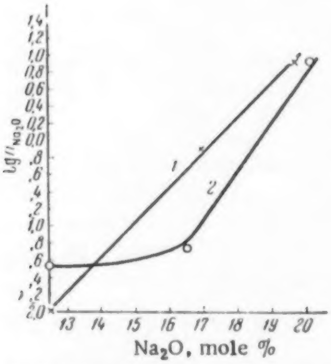

Fig. 2. Dependence of the amount of sodium oxide passed into solution on the sodium oxide content in the glass:

1) $\frac{O}{Si + Al} = 2$; 2) $\frac{O}{Si + Al} = 2.05$.

although 1 : 0.97 : 3.11 glass approaches in its behavior that of the soluble glasses. It may be assumed that the components of 1 : 1 : 3 glass would pass into solution in the same ratio in which they exist in the original glass, i.e., a process of solution would occur.

Passing to the nephelin type glasses, it is possible to note that, as it is evident from the data in Tables 2 and 3, all these practically dissolve when treated with 0.1 N hydrochloric acid: transfer of all components into solution occurs in the same ratio in which they existed in the original glass (α and β close to unity). With increased oxygen number, from 2.04 to 2.09, the values of n_{Na_2O}, $n_{Al_2O_3}$ and n_{SiO_2} are changed but little.

Figure 1 shows the dependence of destructability of the silicon-oxygen skeleton on the oxygen number in two series of glasses: 1 : 1 : 3 and 1 : 1 : 4. On the abscissa axis we located the oxygen number; on the ordinate axis – the values of $\log \frac{n_{SiO_2}}{m}$.

As it is evident from Fig. 1, this dependence for the first series may be expressed by a straight line; the logarithm of the amount of silica passed into solution, as related to its content in the glass, is inversely proportional to the oxygen number of the glass. In the second series, this dependence is preserved only for glasses with oxygen number from 1.98 to 2.05; a further change of the oxygen number practically does not change the course and the rate of destruction of the silicon-oxygen carcass of the glass.

On Fig. 2 is shown the dependence of the passage of sodium oxide from the glass into solution on its content in the glasses with the same oxygen number. On the abscissa axis we located the mole percent of sodium oxide in the glass, on ordinate axis – the values of log (n_{Na_2O}). As it is evident from Fig. 2, this dependence, for glasses with oxygen number equal to 2 with the content of Na_2O in the glasses from 12 to 20 mole %, may be expressed by a straight line: log n_{Na_2O} is directly proportional to the sodium oxide content of the glass. For glasses with oxygen number of 2.04-2.05, this direct proportionality is preserved with the maintenance of sodium oxide in the glass within the limits of 16-20%. A further increase of sodium oxide content, or its decrease, does not materially change the amounts of sodium oxide passed into solution, in comparison with the adjacent compositions.

DISCUSSION OF RESULTS

In the previous studies we examined the acid resistance of glassy sodium aluminosilicates in connection with the combination of the various types of bonds existing in the glass [5]. The most stable links, in respect to resistance to the aggressive action of acids, should be those of silicon–oxygen bound with each other at all apices. The greater is the number of such groups in the glass, i.e., the more polymerized is the silicon–oxygen network, the larger is the amount of aluminum oxide needed to rupture these bonds. It is evident from our data that for a glass which corresponds to trisilicate in its composition, it is necessary to add one mole of aluminum oxide in order that all silica from the decomposed layer pass into solution (α = 1). Only 6-8% of silica passes into solution under the action of hydrochloric acid after the addition of one mole of aluminum oxide to sodium tetrasilicate. At the same time, addition of 0.5 mole of aluminum oxide to glassy sodium bisilicate suffices to make the glass dissolve in hydrochloric acid. The larger is the oxygen number, i.e., the greater is the content of silica relative to alumina, the less influence does the change of sodium oxide content exert on the destructibility of the aluminosilicate glasses. As is

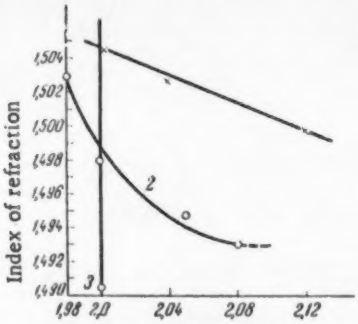

Fig. 3. Dependence of the index of refraction on the oxygen number: 1) glasses of 1 : 1 : 3 type; 2) glasses of 1 : 1 : 4 type; 3) feldspar glass.

evident in Fig. 2, the destructibility is directly proportional to the sodium oxide content in glasses with oxygen number equal to two. For glasses with oxygen number 2.04-2.05, this rule is preserved only within composition interval with relatively higher sodium oxide content. It is possible to see how much the destructibility of aluminosilicate glasses in acids depends on the oxygen number from the comparison of the chemical stability of glasses No. 12 and 2. The oxygen number of the former is 2.12, that of the latter 2.05. Despite the fact that glass No. 12 contains over 20% sodium oxide, while glass No. 2 contains but 13%, their chemical stability is of the same order.

The silicon–oxygen carcass of the nephelin type glasses studied by us is already so depolymerized that the change of the oxygen number within the limits of 2.0-2.09 does not materially alter the rate of their destruction. If one starts with the fact that aluminum in the glasses examined by us is in the state of coordination of four, i.e., the glass carcass is composed by combination of aluminum-oxygen and silicon-oxygen tetrahedra, then for glasses of the nephelin type the greater percentage of the silicon-oxygen groups would be bound at all four apices by the aluminum-oxygen groups. Such groups are the weakest links in the carcass in respect to resistance to the action of acids. Experiments run with glassy sodium aluminosilicates do not permit the conclusion that the coordination number of aluminum changes in these glasses.

Determination of the indexes of refraction of the two series of glasses showed a continuous decline of this index with increasing oxygen number (Fig. 3), which also indicates the presence of aluminum in these glasses in the same coordination state.

SUMMARY

1. The dependence of the acid resistance on the alteration of the oxygen number of sodium aluminosilicate glasses was studied in the region of compositions $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ – $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$.

2. The acid resistance of glasses of feldspar type is practically unchanged with change of the oxygen number. The chemical resistance of glasses of the jadeite types and glasses of 1 : 1 : 3 type increases with increase of the oxygen number.

3. The higher is the oxygen number of sodium aluminosilicate glasses, the smaller effect is produced by the alteration of sodium content in them in respect to their destructibility in acid solutions.

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PHYSICAL CHEMISTRY

CONCERNING ADSORPTIONAL PROPERTIES OF CARBON ADSORBENTS

3. A STUDY OF ADSORPTION ISOTHERMS OF GASES AND VAPORS ON ACTIVE CARBONS OVER A WIDE INTERVAL OF TEMPERATURES, INCLUDING THE CRITICAL REGION

K. M. Nikolaev and M. M. Dubinin

The study of adsorption of the same substances in the gaseous and the vapor states has an important meaning for the development of the theory of physical adsorption. Such studies also permit one to draw conclusions about the properties of substances in the adsorptional layer.

Only a few papers may be classified with the experimental publications devoted to a systematic study of adsorption over a wide temperature range [1- 8]. Even in these few papers the regions of critical temperatures were not always examined and the interval of low equilibrium pressures (under 10 mm of mercury) has always remained unstudied. The selection of the adsorbents, especially active carbons, had as a rule a fortuitous character, while the effect of the structure of the active carbons on adsorption remained unestablished.

The experimental data [1-3] were subjected to a detailed analysis from the viewpoint of the potential theory of adsorption [9-10]. An attempt was made to develop an adsorption theory including the gaseous and the vapor states of substances and to improve the methods of calculation of both the characteristic curves and the adsorption isotherms. In papers [5-6] it was stressed that it is necessary to use the values of corrected molar volumes at temperatures near the critical ones in the calculations made on the basis of the potential theory of adsorption.

It should be noted that the methods developed by these authors, methods which consist of construction of calculated isotherms from the experimental points, are as a whole characterized by clumsiness, complexity and poor suitability to practical usage. No equations for the adsorption isotherms were proposed. It was noted above that the previously accumulated experimental material cannot be considered as being sufficiently complete for the solution of the problem of physical adsorption in both gaseous and vapor states of substances on adsorbents with different porous structures, from a unified viewpoint. All this served as the basis for the setting-up of the present study.

EXPERIMENTAL

Two specimens of active carbons were used in the study, these samples having been prepared under laboratory conditions and being materially different in structure and adsorptional properties. AU1 was a granulated carbon based on coal and wood tar; it was activated by carbon dioxide at the temperature of 950° with burn-off of about 60%. The constants for the equation of the adsorption isotherms of benzene vapors at 20° for the adsorbents of the first structural type [11] were: $W_0 = 0.320$ cm^3/g and $B = 1.07 \cdot 10^{-6}$. AU2 was prepared by thermal decomposition of polyvinylidenechloride with subsequent activation with carbon dioxide with slight burn-off. This carbon, in its properties, was close to that used in paper [12]. For the equation of the adsorption isotherm for benzene vapor at 20°, $W_0 = 0.442$ cm^3/g and $B = 0.425 \cdot 10^{-6}$.

Nitrogen, krypton, xenon, tetrafluoroethylene and hexafluoropropylene were used as the adsorbed substances. Especial attention was paid to the purity of the substances used. The experimentally determined

densities of the saturated vapors agreed well with the tabulated data. The physical constants of the substances, taken for the theoretical analysis of the experimental results, are given in Table 1. Critical temperature t_{cr}, critical pressure p_{cr} and critical density ρ_{cr} for hexafluoropropylene were calculated on the basis of the semi-empirical equations [13]. Constants b of the van der Waals equation were calculated from the formula:

$$b = \frac{1}{8} \frac{RT_{cr}}{p_{cr}} \tag{1}$$

The measurement of the adsorption isotherms over a wide range of equilibrium pressures from $1 \cdot 10^{-3}$ to 700 mm of mercury and temperatures from −195° to +50°, including the critical regions of all substances, was done by the volumetric method on a standard set-up developed in our laboratory. This set-up did not differ in its outline from the known installations using this method. A sample of about 0.5 g of the adsorbent was placed in an ampul made of molybdenum glass, located in a vertical tube electric furnace at the stage of preliminary evacuation or in a cryostat under the operating conditions of the apparatus. The preliminary evacuation of the carbon was done with a three-stage mercury pump for six hours at 450° with attainment of vacuum of the order of 10^{-6} mm (point at which Hg sticks in the capillary of the McLeod gauge). Then the adsorbent was washed at room temperature with the substance being adsorbed and then was again evacuated under the indicated conditions.

Measurements of pressure were made with a McLeod gauge over the range of $1 \cdot 10^{-4}$ to 0.5 mm and with a U-tube mercury manometer for the range of 0.1 to 800 mm. The cathetometer was provided with a helical ocular micrometer, one division of which being equivalent to 0.005 mm. Pressures over 10 mm were measured with the accuracy of 0.1 mm. The measuring part of the apparatus (mercurial gas burettes, manometers) were located in an air thermostat at 30° with automatic temperature regulation within ± 0.1°. The calibration of the measuring part of the apparatus and the determination of the volume of the "dead space" was done with helium.

The ampul with the active carbon in the working state was located in a cryostat which permitted temperature maintenance with the accuracy of ±0.01° in the range from −180° to 50°. The cryostat was constructed in our laboratory on the basis of a circuit in which the automatic temperature regulation was attained through a thyratron thermoregulator with a feedback circuit [14]. The temperature of −195° was maintained with boiling nitrogen.

Special attention was paid during the course of the experiments to the attainment of the equilibrium state. Usually, the adsorptional equilibrium was reached in 30-60 minutes. The values of adsorption were calculated by the usual method, by the use of the equation of state for ideal gases. The adsorption isotherm for each substance was measured not fewer than two times. The results of parallel experiments agreed well.

Families of adsorption isotherms of tetrafluoroethylene and krypton are shown as examples in Figs. 1 and 2 for various temperatures with the two active carbons studied by us. With the scale in use, the initial parts of the isotherms for equilibrium pressures under 1 mm cannot be reproduced on the graphs' abscissae axes. The adsorption isotherms for both substances were determined at temperatures below critical, critical and above critical. The adsorbability of each substance rises considerably with drop in temperature and the isotherms acquire a more curved form. It should be noted that transition through the critical region is not accompanied by a qualitative change of form of the adsorption isotherms. The graph clearly illustrates how considerably does the adsorbability of krypton rise in the gaseous and the vapor states in passing from AU1 to the more finely porous active carbon AU2, i.e., on decrease of constant B of the equation of the adsorption isotherm.

The adsorption isotherms of N_2, Kr, Xe, C_2F_4 and C_3F_6 at temperature of −40° are shown in Fig. 3 on semi-logarithmic coordinates over the entire interval of equilibrium pressures. For nitrogen and krypton the temperature of the experiments was above critical, while for the other substances it was below critical. The adsorbability of the substances over the entire interval of equilibrium pressures studied by us rises qualitatively with in crease of critical temperatures or boiling points at atmospheric pressure. A similar picture is observed for other temperatures for carbons AU1 and AU2.

DISCUSSION OF RESULTS

1. Active carbons of the first structural type [11] are apolar adsorbents with a sharply defined energetic

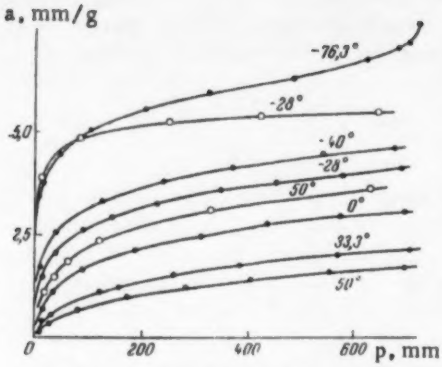

Fig. 1. Families of adsorption isotherms of tetrafluoroethylene on active carbons: ●) AU1; ○) AU2.

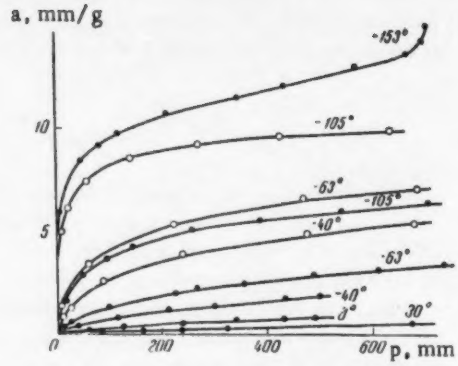

Fig. 2. Families of adsorption isotherms of krypton on active carbons: ●) AU1; ○) AU2.

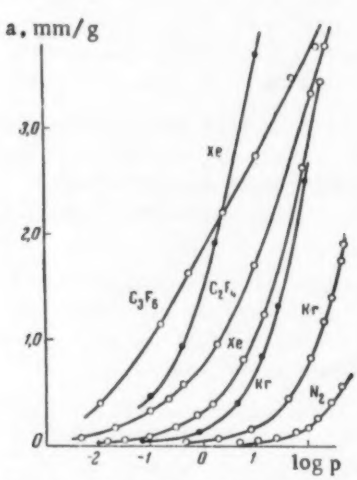

Fig. 3. Adsorption isotherms in semilogarithmic coordinates for temperature of $-40°$: ○) AU1; ●) AU2.

inhomogeneity of the surface [12]. For this reason the adsorption theories developed for adsorbents with a uniform surface (see example [15]) are inapplicable to active carbons. In a series of papers, summarized in [16], the good applicability of the potential theory of adsorption, whose basis was developed by Polanyi [17], to adsorption of gases and vapors on active carbons was proved on experimental basis. A further development of the potential theory permitted the establishment in analytical form of the equations for the characteristic curves and adsorption isotherms for active carbons of limiting structural types [11]. All this serves as a basis for analysis of the experimental data in light of the potential theory of adsorption.

The basic characteristic of the field of adsorptional forces in this theory is the distribution of volume of the adsorptional space W among the adsorptional potentials ϵ, which is expressed by the so-called characteristic curve or equation:

$$\epsilon = f(W). \tag{2}$$

Since the adsorptional potential represents the temperature-independent work of the adsorptional forces, bound by the dispersional interaction of the molecules being adsorbed and the surface of active carbon, then, according to the potential theory, the temperature should not affect the characteristic curve of each system under study: active carbon—substance being adsorbed. This consequence of the theory is confirmed most satisfactorily in an experiment with adsorption of the vapors of the substances at temperatures below their boiling points. In this case, a calculation of the volumes of filled adsorptional space W from the values of adsorption $\underline{a}$ and adsorptional potentials ϵ from relative equilibrium pressures p/p_s is performed with the simplest formulas suggested by Polanyi [17]:

$$W = av; \tag{3}$$

$$\epsilon = 2.30\,RT \log p_s/p, \tag{4}$$

where $\underline{v}$ — volume of a millimole of liquefied gas at the experimental temperature T, if the values of adsorption are expressed in millimoles per gram and R — gas constant.

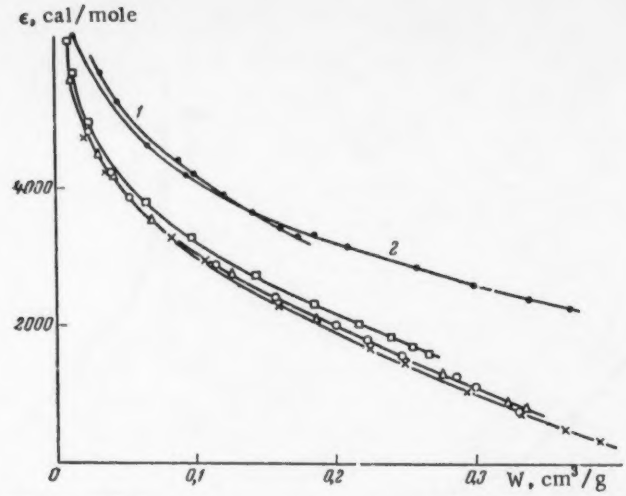

Fig. 4. Characteristic curves of adsorption of tetrafluoroethylene on AU1, calculated from adsorption isotherms for temperatures: ●) 33.3° (critical); □) 0°; ○) −28°; △) −40°; ×) − 76.3°. Curve 1 was calculated with formulas (5) and (6); Curve 2 — with formulas (3) and (4).

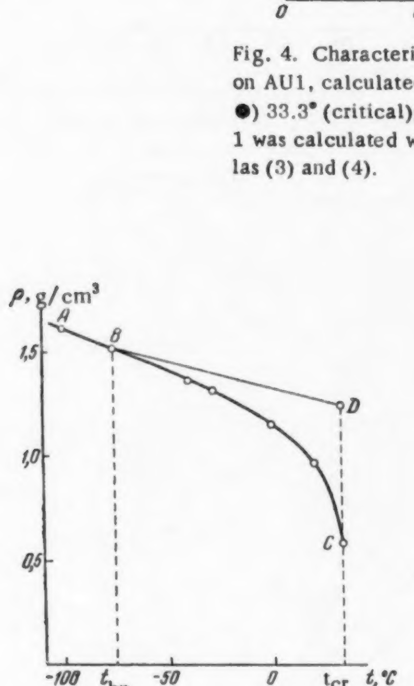

Fig. 5. Dependence of density of liquid tetrafluoroethylene on temperature.

For gases, constant b of the van der Waals equation plays, according to Berenyi, the role of molar volume; semiempirical formula [9, 18] is used for the calculation of the adsorptional potential; then:

$$W = ab; \tag{5}$$

$$\epsilon = 2.30\, RT \log \frac{31.4T}{bp} \tag{6}$$

where constant b is expressed in cubic centimeters per millimole.

The characteristic curves of C_2F_4 on AU1, calculated from the experimental adsorption isotherms with the use of formulas (3) and (4) for temperatures $t \leq t_{cr}$, i.e., for the vapor state of matter in the space* equilibrium phase, and with the use of formulas (5) and (6) for $t > t_{cr}$, i.e., for the gaseous state, are shown as examples on Fig. 4. The characteristic curves for the interval of lower temperatures from −28° to −76.3°, removed considerably from the critical temperature, are practically coincident. A noticeable deviation of the characteristic curve is observed at 0°; the calculated characteristic curve at critical temperature is located considerably higher. Calculations for $t \geq t_{cr}$, by Berenyi's method, yield characteristic curves which are almost coincident with the characteristic curve calculated by Polanyi's method for the critical temperature.

It was mentioned above that the characteristic curve for the system AU1 − C_2F_4 which is being examined, should be a singular one, as one that expresses the invariant, in respect to temperature, distribution of the volume of the adsorptional space among the adsorptional potentials; this follows from the very physical meaning of the characteristic curve. Hence the establishment of the reasons for noncoincidence of the characteristic curves has a fundamental significance.

2. The expressions for adsorptional potentials (4) and (6) were obtained by application of the equation

*Adsorptional space.

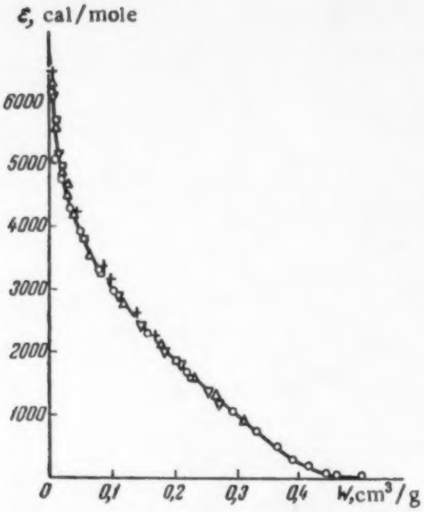

Fig. 6. Characteristic curve of adsorption of tetrafluoroethylene on AU1 calculated from adsorption isotherms at temperatures: + −33.3° (critical); □ −0°; ∇) −28°; Δ) −40°; ○) −76.3°.

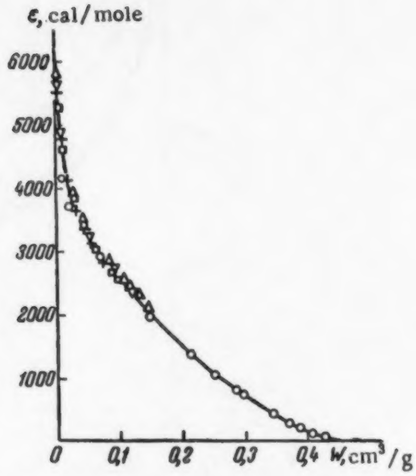

Fig. 7. Characteristic curve of adsorption of xenon on AU1, calculated from adsorption isotherms for temperatures: + −50°; □ −30°; ∇ −16.6° (critical); Δ −0°; ○) −107°.

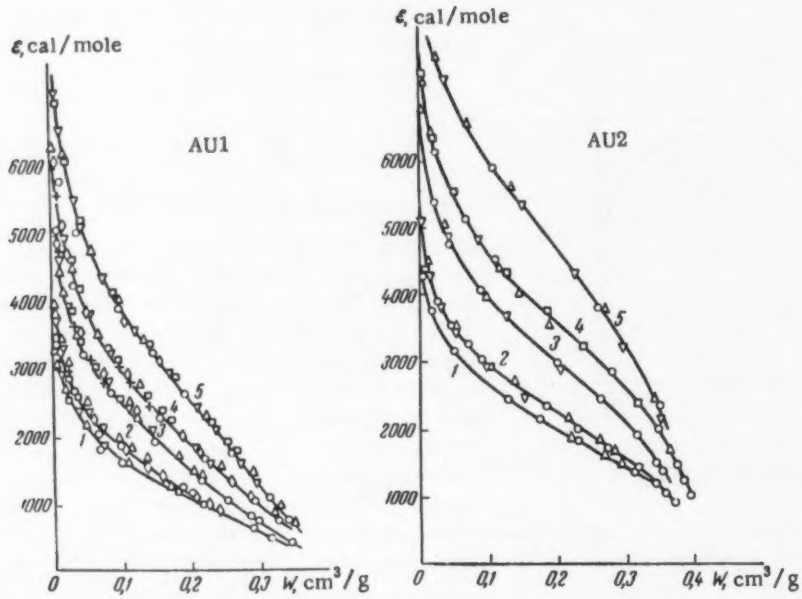

Fig. 8. Characteristic adsorption curves for N_2 (1), Kr (2), Xe (3), C_2F_4 (4) and C_3F_6 (5) on AU1 (left) and AU2 (right).

of state for an ideal gas. The corrections for nonideality of the gas phase are not large, as shown by calculations (see for example [9]), and do not cause any material changes in the values of the adsorptional potentials. Thus the noncoincidence of the characteristic curves in Fig. 4 cannot be explained by the errors caused by the application of the equation of state for an ideal gas.

TABLE 1

Physical Constants of the Substances

Substance	M	B. p. in °C	ρ_{bp} in g/cm³	t_{cr} in °C	p_{cr} in atm	ρ_{cr} in g/cm³	b in cm³/mM
N_2	28,02	—195,8	0,808	—147,1	33,5	0,311	0,0391
Kr	83,70	—152,9	2,115	—63,0	54,0	0,78	0,0398
Xe	131,3	—107,1	3,06	16,6	58,2	1,16	0,0511
C_2F_4	100,0	—76,3	1,52	33,3	38,9	0,58	0,0808
C_3F_6	150,1	—29,4	1,55	71,0	29,3	0,60	0,121

TABLE 2

Affinity Coefficients of Characteristic Curves

Substance	β		Average β
	AU1	AU2	
N_2	1.00	1.00	1.00
Kr	1.11	1.10	1.11
Xe	1.50	1.47	1.49
C_2F_4	1.80	1.75	1.78
C_3F_6	2.31	2.29	2.30

It is known that the adsorbed substance exists in a highly compressed state, on the basis of the preliminary calculations and attempts at direct measurements [19-22]. For temperatures considerably below critical, the compressibility of the liquid in the space phase, and hence in the adsorbed state, may be neglected. In this case it is possible to use the tabular values of liquid density for the experimental temperature during the calculation of the molar volume of the liquid $\underline{v}$, which enters formula (3). The characteristic curves, calculated from the vapor adsorption isotherms, agree well in this temperature interval.

The density of the liquid in the space phase falls sharply during the approach to critical temperature. The dependence of density of liquid tetrafluoroethylene on temperature is shown graphically on Fig. 5 as an example. For temperatures below the boiling point at atmospheric pressure, i.e., in the region AB, the liquid density decreases slowly with temperature in approximately linear manner. The noted sharp fall of the liquid density is characteristic for the curve segment BC.

The adsorbed substance under these conditions exists in greatly compressed state in the field of the adsorptional forces. Since the compressibility of a liquid rises rapidly with approach to the critical temperature, the use of the tabulated values of liquid density, which is permissible for temperatures far removed from critical (practically below the boiling point), ceases to be justified. It is possible to approximate the temperature dependence of the density of the substance in adsorbed state in the temperature interval from t_{bp} to t_{cr} by a linear expression (7);

$$\rho^* = \rho_{bp} - \left(\frac{\rho_{bp} - \rho_m}{t_{cr} - t_{bp}}\right)(t - t_{bp}), \tag{7}$$

where ρ_{bp} – tabulated value of density at t_{bp} and ρ_m – density numerically equal to:

$$\rho_m = \frac{M}{1000\,b}, \tag{8}$$

where $\underline{b}$ – constant of the van der Waals equation in cubic centimeters per millimole (Table 1). This assumption is equivalent to the supposition that the molar volume of substances in the adsorbed state at critical temperature and above is equal to four times the specific volume of the molecules.

Then, for the volume of a millimole of a liquid in the adsorbed state v^* at $t_{bp} < t < t_{cr}$ we have:

$$v^* = \frac{M}{1000\,\rho^*}. \tag{9}$$

The values of molar volumes v^*, calculated by this method, agree quite satisfactorily with the results of another study [8].

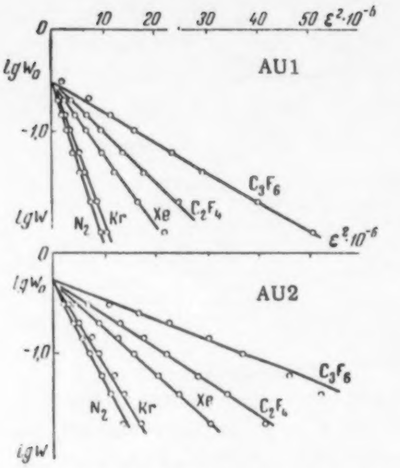

Fig. 9. Characteristic curves of adsorption in linear form from equation (19) for AU1 (top) and AU2 (bottom).

If in the calculation of characteristic curves from the adsorption isotherms for temperatures $t \leq t_{cr}$ one uses formulas (3) and (4) at $v = v^*$ according to (9), then for each system AU-adsorbed substance all the points are distributed sufficiently well on the same characteristic curve. For an example,we give in Fig. 6 the results of calculations from the experiments run with AU1 and C_2F_4. It is possible to conclude that this method of evaluation of density of a substance in the adsorbed state actually does lead to the invariability of the characteristic curve over a wide temperature interval, including the critical region.

Thus, the main cause of deviation of the characteristic curve at $t \leq t_{cr}$ shown in Fig. 4 may be seen to lie in the elevated density of the vapor, liquefied in the carbon pores, elevated in comparison with the liquid density in the space phase.

The semiempirical formula of Berenyi (6) should be corrected in light of these results, the correction being made so that the characteristic curves, calculated from the adsorption isotherms for $t \geq t_{cr}$, would coincide with the already determined singular characteristic curve for the region of vapor state. This may be done by starting with the following considerations. Only for one temperature – namely the critical – should the calculation of the characteristic curve by the method, developed for the vapor and being sought for gases, lead to the same results. Therefore, for equal filling of the volume of the adsorptional space at $T = T_{cr}$ we obtain from the conditions of equality of adsorptional potentials expressed by (4) and from the formula of type (6):

$$RT_{cr} \log \frac{p_{cr}}{p} = RT_{cr} \log \frac{nT_{cr}}{bp}, \tag{10}$$

from which it follows that:

$$n = \frac{p_{cr} b}{T_{cr}}, \tag{11}$$

An analysis of the experimental data on gas adsorption at $t \geq t_{cr}$ permitted us to establish that $\underline{n}$ is not a constant value but depends on temperature. According to the experimental data, the characteristic curves for $t \geq t_{cr}$ coincide with each other well enough and coincide with the singular characteristic curve for $t \leq t_{cr}$ if for $\underline{n}$ we use the following expression:

$$n = \frac{p_{cr} b}{T_{cr}} \tau, \tag{12}$$

where τ – corresponding temperature:

$$\tau = \frac{T}{T_{cr}}. \tag{13}$$

Substituting the value of $\underline{n}$ from (12) for the numerical coefficient 31.4 in formula (6) we obtain the following experimentally refined formulas for the calculation of characteristic curves from the adsorption isotherms of gases on active carbons, if the value of adsorption $\underline{a}$ is expressed in millimoles per gram and equilibrium pressures $\underline{p}$ are given in millimeters of mercury:

$$W = ab \tag{14}$$

$$\epsilon = 2.30\ RT \ \log \tau^2 \frac{p_{cr}}{p}, \tag{15}$$

while for analogous calculation from vapor adsorption isotherms:

$$W = av^*; \quad (16)$$

$$\epsilon = 2.30\,RT \log \frac{p_s}{p}, \quad (17)$$

where for $t < t_{bp}$ we use for v^* the tabulated value of the volume of a millimole of the liquid at experimental temperature, while for the interval $t_{bp} < t < t_{cr}$ – the experimentally refined value from formula (9).

A single characteristic curve of adsorption of xenon on AU1, calculated from adsorption isotherms for temperature interval from $-107°$ to $+50°$, which includes the critical region ($t_{cr} = 16.6°$), is shown as an example on Fig. 7. Similar results were obtained also for the other substances on AU1 and AU2 (Fig. 8). Calculation of the singular characteristic curve from formulas (14) – (17) from experimental data of other authors [1, 6] also led to good results.

3. The equation of the characteristic curve for adsorbents of the first structural type is applicable for the specimens of active carbons studied by us:

$$W = W_0 e^{-k\frac{\epsilon^2}{\beta^2}}, \quad (18)$$

where W_0 – limiting volume of adsorptional space and β – affinity coefficient. This equation has the following form in a linear formula:

$$\log W = E - F\epsilon^2, \quad (19)$$

where

$$E = \log W_0 \quad (20)$$

and

$$F = 0.434 \frac{k}{\beta^2}. \quad (21)$$

The applicability of equation (18) for the all the substances and samples of activated carbons studied by us is illustrated on Fig. 9 for the interval of filling of the volume of the adsorptional space W/W_0 from 0.06 to 0.94. It should be noted that the experimental points, which correspond to the isotherms from all temperatures studied, are located on the straight line for each substance being adsorbed. Graphs of Fig. 9 speak of the good applicability of the equation for the characteristic curve (18). For each carbon all the straight lines intersect the ordinate axis in practically the same point. This indicates, in accord with the theory [23], the constancy of the limiting volumes of the adsorptional space for each specimen of carbon. On the average, we have for AU1 $W_0 = 0.32 \pm 0.01$ cm^3/g and for AU2 $W_0 = 0.53 \pm 0.01$ cm^3/g. Thus, for AU2 the effect of ultraporosity was not manifested for the substances studied,as it was clearly shown in adsorption of benzene on the same carbon ($W_0 = 0.442$ cm^3/g). In agreement with [12], this difference was not seen for the more macroporous carbon AU1.

The coefficients of affinity of the characteristic curves were calculated from constants F according to (21), taking nitrogen as the standard substance (F_N; $\beta = 1$):

$$\beta = \sqrt{\frac{F_N}{F}}. \quad (22)$$

The results of the calculations are given in Table 2.

According to the data in Table 2, the calculated affinity coefficients are practically the same for AU1 and AU2 which belong to the extreme members of the series of samples of active carbons of the first structural type.

By using the Equation (18) of the characteristic curve, Equations (14) and (16) for the filled volumes of the adsorptional space and Equations (15) and (17) for adsorptional potentials, it is possible to obtain the equations for the adsorption isotherms for the substances in gaseous (23) and vapor (24) states, when the values of adsorption would be expressed in millimoles per gram:

$$\text{for gases: } T \geq T_{cr}\text{: } a = \frac{W_0}{b}\, e^{-\left[B\, \frac{T^2}{\beta^2} \left(\log \tau^2\, \frac{P_{cr}}{p}\right)^2\right]}; \tag{23}$$

$$\text{for vapors: } T \leq T_{cr}\text{: } a = \frac{W_0}{v^*}\, e^{-\left[B\, \frac{T^2}{\beta^2} \left(\log \frac{P_s}{p}\right)^2\right]}, \tag{24}$$

where the volume of 1 millimole of liquid v^* for $t < t_{bp}$ is taken from the tables, while for $t_{bp} < t < t_{cr}$ it is calculated from formula (9).

These equations are applicable for the interval of degree of filling of the adsorptional space W/W_0 from 0.06 to 0.94, for substances existing in the vapor state, and with the usual interval of equilibrium pressures (relative) p/p_s from $1 \cdot 10^{-5}$ to 0.1. Smaller values of degree of filling of the volume of the adsorption space may be obtained in the initial region of the isotherms for adsorption of gases, as well as vapors near the critical temperature. According to the experimental data at $W/W_0 << 0.06$ Equations (23) and (24) correspond to the results of measurements for the interval of 1.5 orders of magnitude but with a materially lowered value of the limiting volume of the adsorptional space and smaller value of constant B. Evidently in such cases the determining role for adsorption is possessed by only a part of the volume of the carbon micropores, a part corresponding to the smaller, finer pores for which the effect of increased adsorptional potentials is seen to be quite pronounced. The relative changes of the constants of the equation for the adsorption isotherm, W_0 and B, are in agreement with this supposition in transition into the area of rather low degrees of filling.

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SUMMARY

1. The adsorption isotherms of nitrogen, krypton, xenon, tetrafluoroethylene and hexafluoropropylene were studied over a wide temperature interval, including the critical region, with two specimens of active carbon which belonged to the extreme members of the series of active carbons of the first structrual type.

2. As a result of the analysis of experimental data and of the examination of the peculiarities of the state of adsorbed substances in the region of the critical temperature, rational methods of calculation were proposed for the characteristic curve from adsorption isotherms of the substances in gaseous and vapor states.

3. In accord with the potential theory of adsorption, the affinity coefficients of the characteristic curves do not depend on the structure of the carbon, while the limiting volumes of the adsorptional space are constant magnitudes for each active carbon, provided that the effect of ultraporosity is not manifested.

4. Equations of the adsorption isotherms for active carbons of the first structural type were proposed for gaseous and vapor states of the substances being adsorbed in the equilibrium space phase, these equations corresponding to the same equation of the characteristic curve. These equations of adsorption isotherms were supported experimentally.

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FUNDAMENTAL REGULARITIES OF CATALYTIC OXIDATION OF HYDROCARBONS

1. ADSORPTION OF HYDROCARBONS ON OXIDATIVE CATALYSTS

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The complexity and the many-sided aspect of the process of catalytic oxidation of hydrocarbons have hindered for a long time the clarification of the stepwise mechanism of these reactions. Utilization of the most modern experimental methods permitted the establishment of the main regularities of this process.

Metals and metal oxides – semiconductors – are catalysts for the heterogeneous oxidation of hydrocarbons. The great similarity of the action of these two groups of substances, different in their electronic properties, in the conditions of the oxidation process is evidently explained by the existence of a semiconductor coating on the metal surface [1, 2]. For the clarification of the main regularities of the process, it is necessary to establish the scheme of the oxidation of hydrocarbons, breaking it down into steps. One of the main steps in this process is sorption of the hydrocarbons. Chemosorption of hydrocarbons on various metals (nickel, platinum, copper, etc.) has been studied by many workers [3]. In the latest review by Trapnell [4], devoted to the specificity of catalysis on metals, there are given data on chemosorption of ethylene on various metals and these are interpreted in the light of the role of d-electrons in catalysis and adsorption. However a direct transfer of these regularities to the oxide catalysts is hardly possible. Usually oxygen covers the entire metal surface and the chemosorption of hydrocarbons is realized either on the thin layer of the oxide of the metal, formed as a separate phase, or on oxygen adsorbed on the surface and filling the layers adjacent to the surface. In such cases it is possible to use, with sufficient foundation, the existing data on chemosorption of hydrocarbons on oxides of these metals.

Chemosorption of hydrocarbons on oxide catalysts has been studied but little. Turkevich and Taylor [5] studied the sorption of ethylene, ethane and propane on MoO_2 and Cr_2O_3 over the temperature range 0-400° and separated the regions of purely physical and chemical adsorption. These authors noted the difficulties of study of chemosorption of hydrocarbons on metal oxides owing to the number of side reactions (pyrolysis, oxidation) which occur at the elevated temperatures (200-300°). Some data on chemosorption of unsaturated and paraffinic hydrocarbons on metal oxides, with formation of radicals on the solid surfaces, are cited in the most recent monographs [6] on chemosorption of gases on metal oxides. The oxide surface, if one considers it to be an ideal one, consists of two types of centers of metallic and oxygen ions. Trapnell supposed that the hydrocarbons are not likely bound with oxygen but are sorbed on the metal ions which have an unfilled d-shell. Sorption of ethylene on zinc oxide, in which the metallic Zn^{++} ion has a filled shell, is explained by the formation of a d-s bond.

The absence of experimental data on sorption of hydrocarbons with a simultaneous control of the electronic characteristics of the solid does not allow for the clarification of the true mechanism of chemosorption of hydrocarbons on metal oxides. The goal of our work was the study of chemosorption of hydrocarbons on various oxidative catalysts and the establishment of the role of this step in the oxidative process.

EXPERIMENTAL

Adsorption of hydrocarbons. Sorption of hydrocarbons was studied on typical oxidative catalysts – on metal oxides: vanadium pentoxide, cuprous oxide, nickelous oxide, chromium oxide, magnesium chromite, and on a metal: pure silver coated with oxygen. The characteristics and the methods of preparation of the catalysts are given in Table 1. The purity of all samples was checked by the x-ray method.

TABLE 1

Methods of Preparation and Characteristics of the Catalysts

Catalyst	Method of preparation	Additional treatment	Specific surface in m^2/g
V_2O_5	Decomposition of ammonium vanadate	Heating in oxygen at 450°	12
Cu_2O	Reduction of copper hydroxide with glucose	Annealing at 1000° in nitrogen	8
NiO	Decomposition of nickel carbonate $NiCO_3$	Heating to 900°	1
MnO_2	Electrolysis of $MnSO_4$	Training in vacuum at 250°	56
Cr_2O_3	Precipitation from chromium hydroxide	Heating at 500°	–
Ag	From silver salts	–	0.3

The catalysts were trained in a static vacuum apparatus under a vacuum of 10^{-6} mm at various temperatures. The sorption of hydrocarbons was studied under low pressures by the volumetric method, while for the pressures of 2-200 mm – by means of quartz spring balance. With some samples, the electrical conductivity of the oxide was measured simultaneously with the sorption of hydrocarbons. In this case the catalysts were pressed into tablets under 2000 kg/cm^2 pressure and were placed into a special vacuum reactor with spring electrodes. Electroconductivity was measured by the bridge method. The following hydrocarbons were used as the sorptives: unsaturated ones – ethylene and propylene; saturated - propane.

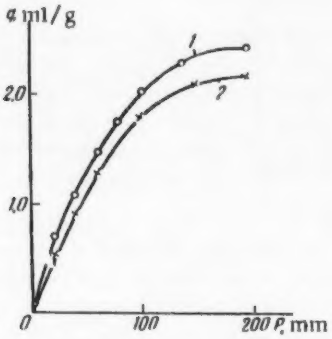

Fig. 1. Sorption isotherms for ethylene on magnesium chromite:
1) primary; 2) secondary at 110°.

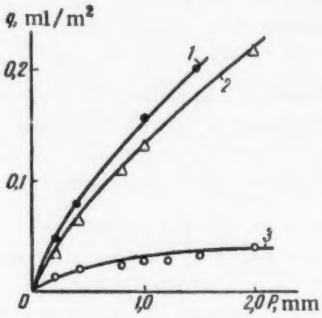

Fig. 2. Sorption isotherms of propylene on nickel oxide (1), vanadium pentoxide (2) and cuprous oxide (3) at 110°

Such conditions were selected for the study of chemosorption in all experiments that the side reactions (oxidation of hydrocarbons by oxygen of the catalyst lattice, decomposition of the hydrocarbon, etc.) were absent. The rates of sorption of hydrocarbons on all the oxide catalysts (V_2O_5, Cu_2O etc.) were very large and the kinetics could not be studied. Figure 1 shows the characteristic "equilibrium" sorption isotherms of ethylene on magnesium chromite.

This is probably a pseudo equilibrium; such a process is only partly reversible at the given temperature and therefore we cannot consider that the hydrocarbon is chemosorbed in equilibrium manner. If one runs successively a sorption of hydrocarbons on the catalyst and a training at a high temperature, the hydrocarbon firmly sorbed on the surface is not removed even in such a case. Only a burning-off with oxygen permits a

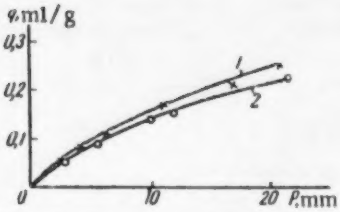

Fig. 3. Sorption isotherms of propylene (1) and propane (2) on cuprous oxide at 100°.

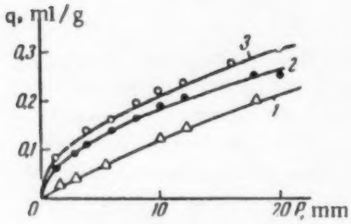

Fig. 4. Sorption isotherms of propylene on cuprous oxide] containing various amounts of copper (1, 2 and 3 increasing copper content).

cleaning of the catalyst surface from the firmly sorbed hydrocarbon. It is interesting to note that, in the absence of the catalytic reaction, the fraction of the firmly sorbed hydrocarbon on the catalyst surface is not over 10% of the total amount sorbed. It is possible to determine the fraction of the firmly sorbed hydrocarbon during the oxidative reaction by analysis of the balance of the oxidation reaction. For magnesium chromite at 350-400° and at low pressures (up to 1 mm) the filling of the surface by strong adsorption amounts to but 1%, while for vanadium pentoxide it is about 5%. Apparently the firmly chemosorbed hydrocarbon serves as the initiator of the side reaction of a chain oxidative polymerization on the catalyst surface, which leads to formation of some organic films containing a large number of carbon atoms. Shekhter and Kushnerova [7] provided electron microscopic data, according to which a coating of high molecular weight hydrocarbons is formed on the surface of vanadium pentoxide during the oxidation of propylene. The active form which carries on the oxidative process is probably the more weakly chemosorbed hydrocarbon.

Isotherms of sorption of propylene on nickelous oxide (NiO), vanadium pentoxide (V_2O_5) and cuprous oxide (Cu_2O) at 100° are given in Fig. 2. All these isotherms are satisfactorily described by the Freundlich equation $q = ap^{1/n}$ and correspond, as shown by Roginskii [8] to inhomogeneous surface with exponential distribution of the heats of adsorption. In Table 2 are shown the degrees of filling of the surface of various metal oxides during sorption of hydrocarbon at 100°. Half of V_2O_5 surface is occupied by propylene at the same pressure at which only 15-17% of cuprous oxide and magnesium chromite are covered by propylene (calculated as a monolayer).

The sorption isotherms of propylene and propane on cuprous oxide at 100° are shown in Fig. 3. Such close quantitative values of chemosorption indicate the high probability of rupture of similar bonds in these molecules, which are so different in their structures. Probably, the bond of hydrogen with the catalyst surface is formed at the methyl group. The close similarity in the character of the isotherms of propane and propylene must be explained, evidently, by the formation of similar intermediate forms during adsorption, specifically by rupture of the C—H bond in the methyl group.

Intermediate forms in hydrocarbon adsorption. According to the electronic theory of chemosorption [2, 9, 10], the appearance of chemosorbed molecules on the semiconductor surface leads to a surface charge. The adsorption of the acceptor molecules causes an increase, and that of donor molecules a decrease, of the escape work, from which alteration one may judge the nature of the adsorbed molecules. Chemosorption may also cause a noticeable change in the electrical conductivity of the semiconductor. Thus, for example, in case of a p-semiconductor, the chemosorption of acceptor molecules leads to an increase, and that of donor molecules to a decrease of the electrical conductivity. The experimental results of measurement of the escape work and of the electroconductivity of various metal oxides after chemosorption of hydrocarbons in the region of admixtural conductivity are shown in Table 3. It was shown by special experiments that reduction of the catalyst surfaces in adsorption was totally absent.

On typical p-semiconductors, the hydrocarbons during sorption lower the electrical conductivity, and, hence, a molecule of a hydrocarbon that is chemosorbed on the surface fulfills the donor role. If the mechanism of conductivity is known, it is possible to state on which of the ions of the lattice the hydrocarbon is sorbed. Thus, in case of nickelous oxide, where the conductivity is determined by the appearance of Ni^{+++} ion, the hydrocarbon molecule by yielding its electron to the lattice changes the Ni^{+++} ion into the Ni^{++} ion. Thereupon, according to the electronic concepts, the valence-saturated molecule is changed into a surface, positively charged ion-radical [2, 9]. Cuprous oxide is an exception as a characteristic hole semiconductor on which the hydrocarbon does not lower but does raise the electrical conductivity in adsorption, i.e., playing the role of an

TABLE 2

Filling of Metallic Oxide Surfaces During Chemosorption of Hydrocarbons

Catalyst	Of a hydrocarbon	Filling, single-layer, %	Pressure, mm, Hg
V_2O_5	C_3H_6	45	2,0
Cu_2O	C_3H_6	17	2,0
$MgCr_2O_4$	C_3H_6	15	2,0

electron acceptor. However a measurement of the escape work of Cu_2O in propylene adsorption shows that the hydrocarbon molecule is charged positively and is an electron donor. Thus, the same molecule of the hydrocarbon acts as a donor in adsorption on NiO, MnO_2, Cr_2O_3 and Cu_2O.

It is interesting to compare the catalytic action and the selectivity of these semiconductors in respect to the catalytic oxidative reaction. Selective oxidation of propylene without the rupture of the double bond is observed only on cuprous oxide. On all other oxidative catalysts (NiO, Cr_2O_3, MnO_2) the unsaturated and the paraffinic hydrocarbons are oxidized with total destruction of the molecule and with formation of final oxidation products: CO_2 and H_2O. An analysis of the experimental data on oxidation of aliphatic hydrocarbons over various metal oxides (V_2O_5, Cu_2O etc.) shows that the reaction products consist of several characteristic types of oxygen-containing compounds, in addition to carbon monoxide and carbon dioxide: 1) aldehydes and acids containing a smaller number of carbon atoms than the initial hydrocarbon molecule, 2) unsaturated aldehyde with the number of carbon atoms corresponding to the olefin hydrocarbon being oxidized (such a reaction occurs on Cu_2O). Acrolein is barely formed on vanadium pentoxide or nickelous oxide. If one oxidizes a hydrocarbon molecule with two double bonds, such as butadiene on V_2O_5 (from data of Bretton, Shen-Wu-Wan and Dodge [14]), methylacrolein is formed – an unsaturated aldehyde with four carbon atoms. Consequently, the direction of the oxidative reaction is connected not only with the character of the free valence (hole or electron) of the solid as supposed by Vol'kenshtein [9], but is also related to the structure of the hydrocarbon molecule being oxidized.

TABLE 3

Charging of the Surface in Hydrocarbon Chemosorption

	Catalyst					
	p-semiconductor				n-semiconductor	
	NiO	Cr_2O_3*	MnO_2	Cu_2O	V_2O_5	ZnO
Hydrocarbon	propylene, propane	butane	ethane	propylene, propane	propylene, propane, xylene**	propylene
Electroconductivity	lowering	lowering	lowering	elevation	elevation	elevation
Sign of charge from electroconductivity	+	+	+	–	+	+
Sign of charge from escape work***	+	not measured	not measured	+	+	+
State of the molecule	donor	donor	donor	donor	donor	donor

*From Weisz' data [11].

**From Clark and Berets' data [12].

***From Enikeev's data [13].

Speaking otherwise, ion-radicals with different structures are formed on the catalyst surface depending on the rupture of the various bonds in the molecule and these determine the various directions of the oxidative process.

Effect of addends* introduced into the catalyst on hydrocarbon sorption. Introduction of addends to the

*Added substances.

oxidative catalysts sharply changes the rates of the oxidation reactions of hydrocarbons and also their selectivity. Thus, introduction of sodium silicate into magnesium chromite ($MgCr_2O_4$) or tungsten oxide WO_3 changes the activation energy of catalytic oxidation from 8 to 40 kilocal/mole with a simultaneous and symbasic change of the preexponential multiplier [15]. The destruction of the stoichiometry of a given substance, i.e., enrichment or impoverishment of it by a metal or a metalloid, serves as another method of introduction of addends to oxides. The addends alter not only the catalytic activity of the semiconductors, but also the adsorptional ability.

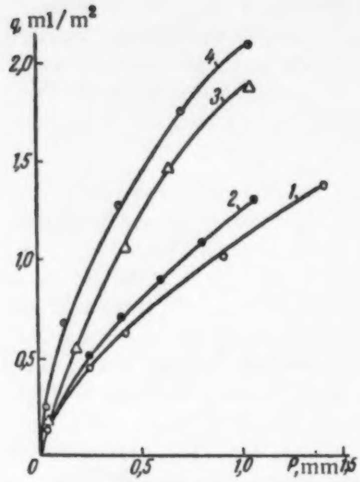

Fig. 5. Sorption isotherms (in ml/m^2) of ethylene on magnesium chromite with addition of sodium silicate. (1 – pure $MgCr_2O_4$; 2 - $MgCr_2O_4$ + 1% Na_2SiO_3; 3 - $MgCr_2O_4$ + 2% Na_2SiO_3; 4 - $MgCr_2O_4$ + 3% Na_2SiO_3) at 110°.

The effect of addends on hydrocarbon sorption was studied with a typical catalyst for mild oxidation – cuprous oxide (samples with different copper content) and with a catalyst for deep oxidation ($MgCr_2O_4$) – magnesium chromite, following the introduction of sodium silicate.

The change of the sorptional ability of cuprous oxide relative to propylene with increased content of the metal in the oxide is shown in Fig. 4. The enrichment of cuprous oxide with the metal leads to an increase of the sorptional ability. For nickelous oxide, however, the greater nickel content brings about a decrease in the sorptional ability. Thus the composition of the oxides has a material effect on the magnitude of hydrocarbon sorption. By introduction of a donor or an acceptor addend into the oxidative catalyst, it is possible to increase the surface concentration of the ion-radicals of the hydrocarbons, i.e., to raise or to lower the concentration of the active forms which carry the oxidative process. On Fig. 5 are shown the sorption isotherms for ethylene and four samples of magnesium chromite with additions of sodium silicate.

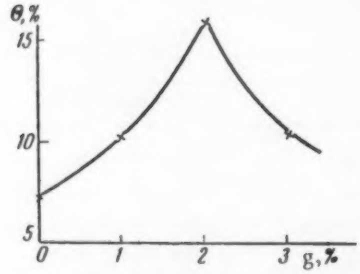

Fig. 6. Degree of filling of the surface by weakly sorbed hydrocarbon on magnesium chromite with added sodium silicate at p = 1.5 mm.

It was shown above that the fraction of the firm sorption of hydrocarbons on oxide surfaces is small in comparison with the reversible weak chemosorption. Introduction of an addend into the catalyst changes the proportion of the strong and the weak sorption (Table 4). With increased amount of sodium silicate in the catalyst, the fraction of the strong chemosorption rises and that of weak hydrocarbon sorption declines.

The change of the degree of filling of the catalyst surfaces containing the addends, by weakly sorbed hydrocarbon at pressure of 1.5 mm and temperature of 110° is shown in Fig. 6. With increasing concentration of the addends, the curves of surface filling by weakly sorbed hydrocarbon pass through a maximum. At a low content of the addend in the catalyst, the catalyst surface is filled with the weakly sorbed hydrocarbon which reaches a maximum corresponding to a certain content of the addend in the catalyst. A further increase of the amount of the addend to the solid leads to a relative increase of the strongly sorbed hydrocarbon, a decline of the weak fraction and the fall of the curve of filling with the weakly sorbed hydrocarbon. It is interesting that the rate of the oxidation reaction of ethylene also passes through a maximum with alteration of the content of the addend in these catalysts.

The catalyst on which the greatest amount of weak hydrocarbon sorption is observed has the maximum catalytic activity. If the strongly sorbed hydrocarbon does not take part in the oxidation reaction, the fraction of the strongly sorbed hydrocarbon, which blocks the active centers of the surface, increases with increased concentration of the addend and the rate of oxidation declines. The increase of the catalytic activity after an introduction of small amounts of the addend must be evidently explained by an increase of the number of centers

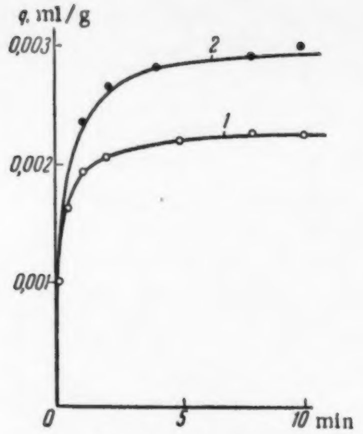

Fig. 7. Adsorption isotherms for ethylene on silver coated with oxygen: 1) at 75°; 2) at 130°.

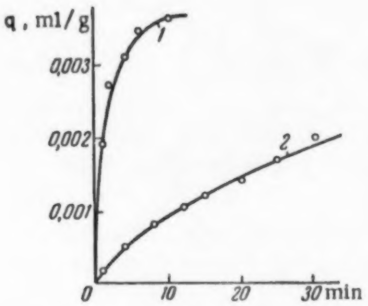

Fig. 8. Primary (1) and secondary (2) adsorption isotherms for ethylene on silver, coated with oxygen, at 130°.

for the weakly sorbed hydrocarbon owing to the change of the electronic properties of these regions of the surface. However it is impossible to explain the sharp rise of the activation energy of the catalytic oxidation of hydrocarbons after a modification of the catalysts simply by the increased number of the adsorptional centers. For inhomogeneous surfaces with an exponential distribution function of the heats of adsorption ρ (Q) = $He^{-\alpha Q}$ (where Q – heat of sorption, α – coefficient of inhomogeneity) the distribution changes gradually to a sharp and narrow peak, i.e., approaches the homogeneous surface, with increased value of the power coefficient. The surface approaches the uniformly inhomogeneous one with decreased α. The change of the inhomogeneity coefficient α of the surface of magnesium chromite after introduction of sodium silicate, for summary adsorption of propylene, is shown in Table 5.

With increasing amount of the addend in magnesium chromite, the inhomogeneity coefficient of the surface becomes smaller, probably, owing to the origination of centers for strong adsorption of hydrocarbons. Consequently, the inhomogeneity of the surface rises. It is possible to suppress or to strengthen the formation of strongly sorbed hydrocarbon, which lowers the catalytic activity of the catalyst in respect to the oxidation reaction, by introduction of the addends.

Sorption of ethylene on silver. The chemosorption of ethylene on pure silver and on silver coated with oxygen was studied for a comparison with sorption of hydrocarbons on metal oxides. According to literature data, ethylene is just barely sorbed on silver at temperatures of 100-250° [16]. On the silver surface, completely freed of oxygen, ethylene is sorbed reversibly and under equilibrium conditions. An entirely different picture is observed in hydrocarbon sorption on silver, coated with oxygen (Fig. 7). The adsorption kinetics is described by Roginskii-Zel'dovich equation which is characteristic for inhomogeneous surface: $w = w_0(-\alpha q)$, where w – rate of sorption and q – amount of sorbed hydrocarbon. In the study of oxidation of propylene on platinum, Butiagin and Elovich [17] showed that the surface of platinum coated with oxygen absorbs propylene and that the rate of this process obeys the same law.

Only a part of ethylene is removed from silver by evacuation and a considerable fraction of sorbed ethylene enters a strong bond with the oxygen of the surface (Fig. 8). The activation energy of the process is very small and amounts to 2-3 kilocal/mole. In cases of sorption on a metal, coated with oxygen, the inhomogeneity of the surface is sharply brought out, probably owing to the formation on the metal surface of areas with different electronic properties. Such an alteration of the properties of the metallic surface is connected with the different state of of oxygen on the silver surface [18]. It is possible that the hydrocarbon that is less strongly bound with the surface is the reactive one on the surface of metal-oxygen,as in oxide catalysts.

The numerous studies made by Surman [19] on the alteration of the resistance of metallic films under the influence of adsorption, showed that dipoles with different direction of the dipole moment are formed by the adsorbed molecules of various gases on the surface. Studies by Twigg [20] and by Liubarskii [21] showed the connection between the electroconductivity of glass threads coated with a silver film, oxygen sorption and reactions of ethylene oxidation. According to our data, the electroconductivity of a very thin silver wire coated with oxygen under the influence of ethylene adsorption is increased. Therefore, the ethylene molecule acts as a donor of an electron; it is charged positively on the surface and, probably, forms a charged ion-radical.

TABLE 4

Ratio of Strong and Weak Sorption of Hydrocarbons on Magnesium Chromite with Added Na_2SiO_3

Catalyst	Addend, in 1	Ratio of sorbed C_3H_6, in %	
		of strong sorption	of strong sorption
$MgCr_2O_4$	0	3	97
$MgCr_2O_4$	1	10	90
$MgCr_2O_4$	2	25	75
$MgCr_2O_4$	3	50	50

TABLE 5

Coefficient of Inhomogeneity α of the Surface of Magnesium Chromite with Added Sodium Silicate for Adsorption of Propylene

Catalyst	Added Na_2SiO_3, in %	Coefficient of inhomogeneity
$MgCr_2O_4$	0	$9.15 \cdot 10^{-4}$
$MgCr_2O_4$	2	$8.57 \cdot 10^{-4}$
$MgCr_2O_4$	3	$6.4 \cdot 10^{-4}$

Thus, on the surface of semiconductors (metal oxides) and on the surface of silver coated with oxygen, the hydrocarbon is transformed into reactive ion-radicals which probably are the basic intermediate forms which carry the catalytic oxidation on solid surfaces. Depending on the chemical properties of the elements which compose the catalysts, and on the character of their electronic properties, as well as on the structure and bond type in the hydrocarbon molecules, there are formed radicals of different structures, which fact leads to the various directions of the oxidative process. In all the systems studied by us, there is observed a weak reversible and a strong fixation of hydrocarbon on the surface. The latter decreases the catalytic activity of the catalysts. Introduction of addends into the catalysts changes the proportion of the weak and the strong sorption on the surface of oxidation catalysts.

SUMMARY

1. Sorption of unsaturated (ethylene, propylene) and saturated (propane) hydrocarbons on various catalysts (V_2O_5, NiO, Cu_2O and $MgCr_2O_4$) was studied.

2. Two types of sorption of hydrocarbons on the surface of metal oxides were established: weak and reversible, which acts as a step in the oxidative reaction, and a strong and irreversible one, which blocks the surface.

3. The effect of chemosorbed hydrocarbon on electroconductivity of the indicated metal oxides was studied and a theory was expressed about the formation of various ion-radicals on the surface of oxidative catalysts after adsorption.

4. The action of addends introduced into $MgCr_2O_4$ and Cu_2O on the sorption of unsaturated hydrocarbons was studied.

5. A similarity was shown in the character of sorption of ethylene on metal oxides and on silver coated with oxygen.

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KINETIC DETERMINATION OF BOND ENERGY WITH CHROMIUM OXIDE CATALYST

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In the present work we studied the kinetics of dehydrogenation and dehydration of isopropyl alcohol and dehydrogenation of cyclohexane over chromium oxide, prepared by heating ammonium bichromate, with the goal of determination of the energies of bonding of the reacting atoms in the molecule with the catalyst. We determined the relative adsorptional coefficients of acetone and hydrogen and calculated the true activation energies of the reaction of dehydrogenation of isopropyl alcohol. Earlier we determined the energies of bonding on chromium oxide prepared by precipitation of chromium nitrate [1-3].

EXPERIMENTAL

The kinetic experiments were run in common apparatus of the flow type. The substance was automatically delivered into the catalytic tube at a constant rate. The gaseous reaction products, the rate of evolution of which was used to judge the reaction rate, were collected in a gasometer with a constant lower level. All gas volumes were reduced to STP. The temperature of the electric heater was maintained constant with accuracy of 1°. The end of the chromel-copel thermocouple well was located in the middle of the catalyst layer, while the thermocouple was connected to a potentiometer. The gaseous reaction products were analyzed in a VTI apparatus.

The finely powdered (in a mortar) ammonium bichromate was poured in a thin layer into a porcelain dish, for preparation of the catalyst, and was heated with a small burner flame. The resulting chromium oxide having the form of green scales, was heated in a current of hydrogen to 200° for 1 hour, to 300° for 1 hour, to 300° for 1 hour and to 400° for 6 hours. One g of the catalyst was placed in the tube; the catalyst volume was 10 ml; length of the catalyst layer was 6 cm.

Starting materials: cyclohexane, b. p. 80° (741 mm), $n^{20}D$ 1.2466; $d^{19.5}_4$ 0.7798 (formalite reaction negative). Isopropyl alcohol, b. p. 81-81.5° (748 mm), $n^{20}D$ 1.3780, d^{20}_4 1.7903; acetone, b. p. 55° (749 mm), $n^{20}D$ 1.3580, d^{20}_4 0.7910.

Dehydrogenation of cyclohexane was studied over the temperature range of 420-460° at supply rate of 0.20 ml/min. The gaseous reaction products consisted of pure hydrogen; in the liquid products (catalyzate) we determined the content of unsaturates (cyclohexene) by the method of bromine number, while the content of benzene was judged from the index of refraction. The degree of conversion of cyclohexane, calculated from hydrogen and benzene, differed but not over 1%. The experimental results are given in Table 1.

The activation energy of the reaction of dehydrogenation of cyclohexane was calculated from the number of milliliters of hydrogen evolved in one minute (ml/min), for calculation of $\log k_0$ by the formula: $\log k_0 = \log m + \frac{\epsilon}{4.57T}$ where $\underline{m}$ is expressed in milliliters of gas evolved in one minute per one ml of the catalyst (ml/min · ml cat). The experimental points of the dependence of log m on $\frac{1}{T}$ fit a straight line well (Fig. 1). Activation energy of dehydrogenation of cyclohexane: $\epsilon_{H_2} = 31.4$ kilocal per mole.

Dehydrogenation and dehydration of isopropyl alcohol were studied over the temperature interval of 260-300° in two series of experiments. The gaseous reaction products consisted only of hydrogen and propylene. The results of the first series of experiments are collected in Table 2. The activation energy of the reaction of dehydrogenation of isopropyl alcohol: $\epsilon_{H_2} = 19.2$ kilocal/mole; activation energy of reaction of dehydra-

TABLE 1

Dehydrogenation of Cyclohexane over Cr_2O_3
(feed rate of 0.20 ml/min; catalyst volume 10 ml; A_1 = 11.68 ml/min·ml of catalyst; ϵ_{H_2} = 31,400 cal/mole)

No. of expt.	Temperature in °C	m_{H_2} in ml/min·ml of catalyst	log k_0	$\frac{\epsilon}{\log k_0}\cdot 10^{-3}$	m_{H_2} calculated from ϵ_{H_2} = 31.4	Analysis of catalyzate in weight %: C_6H_6	Analysis of catalyzate in weight %: C_6H_{10}
2	437	1.175	9.75	3.23	1.186	9.4	1.23
3	444	1.631	9.77	3.22	1.574	13.0	1.39
6	444	1.531	9.75	3.23	1.574	12.2	–
4	452	1.929	9.77	3.22	1.897	15.4	1.38
7	455	2.215	9.80	3.21	2.023	17.7	–
5	458	2.323	9.76	3.22	2.296	18.6	1.38

Average log k_0 = 9.76; $k_0 = 5.75\cdot 10^9$; $\frac{\epsilon_{H_2}}{\log k_0}\cdot 10^{-3} = 3.23$.

TABLE 2

Dehydrogenation and Dehydration of Isopropyl Alcohol
(feed rate 0.20 ml/min; catalyst volume 10 ml; A_1 = 5.89 ml/min·ml·catalyst; ϵ_{H_2} = 19,200 cal/mole; ϵ_{H_2O} = 33,000 cal/mole; catalyst: Cr_2O_3 (first series of experiments)

No of expt.	Temperature of expt. in °C	Dehydrogenation: m_{H_2} in ml/min·ml cat	Dehydrogenation: log k_0	Dehydrogenation: $\frac{\epsilon_{H_2}}{\log k_0}\cdot 10^{-3}$	Dehydrogenation: m_{H_2} calc. from ϵ_{H_2} = = 19.2	Dehydration: $m_{C_3H_6}$ in ml/min·ml cat	Dehydration: log k_0	Dehydration: $\frac{\epsilon_{H_2O}}{\log k_0}\cdot 10^{-3}$	Dehydration: $m_{C_3H_6}$ calc. from ϵ_{H_2O} = = 33.0
2	262	0.32	7.36	2.61	0.33	0.05	12.20	2.70	0.05
18	267	0.36	7.34	2.62	0.40	0.06	12.16	2.71	0.06
5	270	0.45	7.39	2.60	0.42	0.07	12.15	2.71	0.07
7	271.5	0.48	7.40	2.60	0.45	0.08	12.17	2.70	0.08
12	271.5	0.45	7.37	2.61	0.45	0.08	12.17	2.70	0.08
14	278	0.58	7.39	2.60	0.56	0.12	12.19	2.70	0.12
1	280	0.60	7.37	2.61	0.60	0.13	12.16	2.71	0.13
3	280	0.60	7.37	2.61	0.60	0.13	12.16	2.71	0.13
15	283	0.68	7.39	2.60	0.65	0.16	12.19	2.70	0.16
9	291	0.83	7.37	2.61	0.83	0.23	12.16	2.71	0.23
16	291	0.89	7.40	2.60	0.83	0.25	12.20	2.70	0.23
6	296	0.99	7.38	2.60	0.93	0.30	12.16	2.71	0.29
17	299	0.95	7.32	2.62	1.07	0.32	12.12	2.72	0.36
11	307	1.08	7.28	2.64	1.35	0.44	12.10	2.72	0.57

Average log k_0 = 7.37; $k_0 = 2.34\cdot 10^7$; $\frac{\epsilon_{H_2}}{\log k_0}\cdot 10^{-3} = 2.61$.

Average log k_0 = 12.16; $k_0 = 1.44\cdot 10^{12}$; $\frac{\epsilon_{H_2O}}{\log k_0}\cdot 10^{-3} = 2.71$.

tion of isopropyl alcohol: ϵ_{H_2O} = 33.0 kilocal/mole. The second series of experiments was run after extended work with the catalyst, when the latter had reduced its activity. Here the proportion of hydrogen and unsaturates in the gaseous reaction products was different. The gas did not contain any other products, as before, other than hydrogen and propylene. The experimental data from the second series of experiments are given in Table 3.

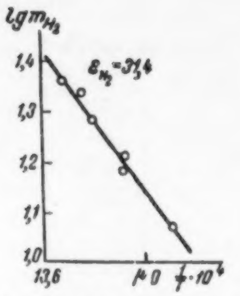

Fig. 1. Dehydrogenation of cyclohexane.

and Fig. 3: ϵ_{H_2} = 17.4 kilocal/mole; ϵ_{H_2O} = 30.5 kilocal/mole. It is evident that the decrease of activity was accompanied by decreased activation energies of both reactions and of the preexponential factors k_0.

Determination of relative adsorptional coefficients of hydrogen and acetone. In order to determine the relative adsorptional coefficients on the catalyst with new activity, we studied the kinetics of decomposition of the alcohol in the presence of products of the dehydrogenation reaction: hydrogen and acetone. It turned out that the presence of hydrogen does not cause any reduction of the rate of dehydrogenation (Table 4). Thus, the relative adsorptional coefficient of hydrogen $z_3 = 0$. The relative adsorptional coefficients of acetone z_2 were calculated for the case in which $z_3 = 0$, by the exact method proposed by one of us [4]. Balandin's general kinetic equation [4] for the case of dehydrogenation (dehydration) of alcohols with participation of one of the reaction products takes the form:

$$[A_1(z_2+z_3)+z_2A_2]\ln\frac{A_1}{A_1-m}-\\-(z_2+z_3-1)=k. \tag{1}$$

In our case when $z_3 = 0$, Equation (1) solved relative to $\ln A_1/(A_1-m)$ takes the form:

$$\ln\frac{A_1}{A_1-m}=\frac{z_2-1}{z_2}(A_1+A_2)m+\\+\frac{k}{z_2(A_1+A_2)}, \tag{2}$$

where A_1 – rate of entry of alcohol into the tube, A_2 – rate of entry of acetone into the tube, m – rate of hydrogen evolution, z_2 – relative adsorptional coefficient of acetone, k – reaction rate constant. $A_1 + A_2$ is constant from one experiment to another and is equal to 5.89 ml/min·ml cat (A_1 and m are expressed in the same units: milliliters of hydrogen corresponding to 100% conversion of the alcohol in one minute per 1 ml of catalyst).

TABLE 3

Dehydrogenation and Dehydration of Isopropyl Alcohol
[catalyst Cr_2O_3 (new activity); feed rate 0.2 ml/min; A_1 = 5.89 ml/min·ml cat; catalyst volume 10 ml; ϵ_{H_2O} = 30.5 kilocal/mole; ϵ_{H_2} = 17.4 kilocal/mole].

Temperature in °C	Dehydrogenation				Dehydration			
	m_{H_2} in ml/min·ml cat	$\log k_0$	$\frac{\epsilon}{\log k_0}\cdot 10^{-3}$	m_{H_2} calc. from ϵ_{H_2} = 17.4	$m_{C_3H_6}$ in ml/min·ml cat	$\log k_0$	$\frac{\epsilon_{H_2O}}{\log k_0}\cdot 10^{-3}$	$m_{C_3H_6}$ calc. from ϵ_{H_2O} = 30.5
275	0.40	6.55	2.66	0.38	0.10	11.12	2.74	0.087
283	0.48	6.52	2.67	0.49	0.14	11.15	2.74	0.14
291	0.60	6.54	2.66	0.59	0.22	11.17	2.73	0.19
299	0.76	6.53	2.67	0.76	0.30	11.13	2.74	0.31

Average $\log k_0$ = 6.53
$k_0 = 3.39\cdot 10^6$; $\frac{\epsilon_{H_2}}{\log k_0}\cdot 10^{-3} = 2.7$.

Average $\log k_0$ = 11.14; $k_0 = 1.39\cdot 10^{11}$;
$\frac{\epsilon_{H_2O}}{\log k_0}\cdot 10^{-3} = 2.74$

Placing the values of $\log A_1/(A_1-m)$ on the ordinate axis and those of m on the abscissae axis, we obtain the straight line (Fig. 4) whose initial ordinate is:

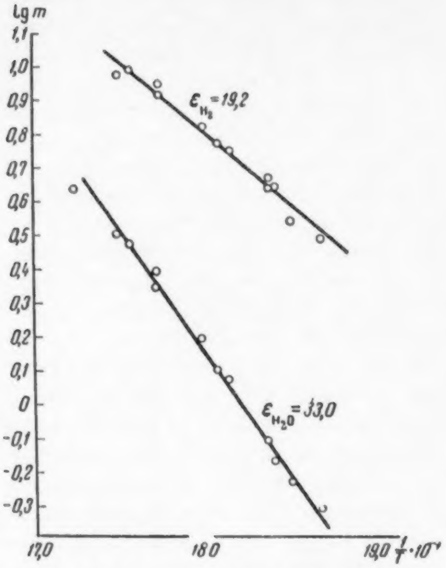

Fig. 2. Dehydrogenation and dehydration of isopropyl alcohol.

$$a = \frac{k}{z_2(A_1 + A_2)\cdot 2.303}, \tag{3}$$

and the angular coefficient is:

$$\gamma = \frac{z_2 - 1}{Z_2(A_1 + A_2)\cdot 2.303}, \tag{4}$$

from which z_2 and $\underline{k}$ may be found. In addition, knowing the value of z_2, it is possible to determine the values of $\underline{k}$ for various temperatures by the following formula:

$$A_1 z_2 \ln \frac{A_1}{A_1 - m} - (z_2 - 1)\, m = k \tag{5}$$

The experimental data on decomposition of mixtures of isopropyl alcohol and acetone are given in Table 5. As in the case of the decomposition of the pure alcohol, the gaseous reaction products consisted only of hydrogen and propylene. Values of z_2, calculated by formula:

$$z_2 = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1}, \tag{6}$$

used previously in papers [5, 6], are given in Table 5. Values of z_2, calculated from Equations (3) and (4) on the basis of the graph (Fig. 4), are given in Table 6.

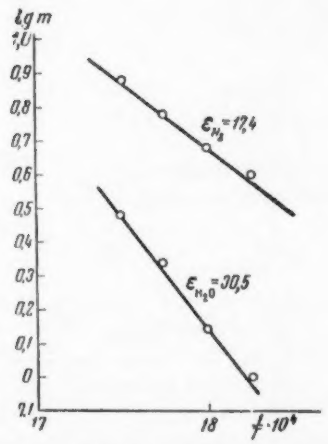

Fig. 3. Dehydrogenation and dehydration of isopropyl alcohol (second series of experiments).

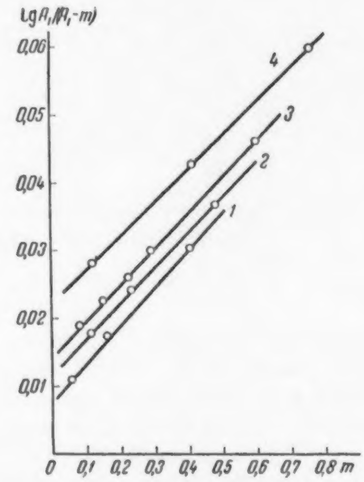

Fig. 4. Dehydrogenation of mixtures of isopropyl alcohol–acetone at various temperatures:
1) 275°; 2) 283°; 3) 231°; 4) 299°.

On the basis of data from this work, we calculated the difference in heats of adsorption of acetone and isopropyl alcohol ΔH, the change in free energy ΔF and the entropy changes ΔS [7] in the adsorptional displacement on the catalytically active centers (Table 7).

Determination of true rate constants and true activation energy of the reaction of dehydrogenation of isopropyl alcohol. Values of k, obtained from Expressions (3) and (4) and from Formula (5) are compared in Table 6. The dependence of log k on 1/T is shown in Fig. 5. True activation energy of dehydrogenation of isopropyl alcohol (first series of experiments) ϵ_{true} = 16.9 kilocal/mole; apparent activation energy ϵ_{H_2} = 17.4 kilocal/mole. Considering the surface of our catalyst as being quasihomogeneous [8], we may by using values of z_2, obtained from the second series of experiments, calculate the values of k with Formula 5) for the first series of experiments (Table 8, Fig. 5). This calculation gave ϵ_{true} = 20.4 kcal/mole, while ϵ_{H_2} = 19.2 kilocal/mole. As shown by the comparison of the apparent and the true activation energies, the difference between them is not great and amounts to but 1.2 kilocal/mole in the first series of experiments and 0.5 kilocal/mole in the second series. Thus working with small conversion percentages (up to 30) it is possible to regard the order of the reaction as being approximately zero. This result agrees with the data obtained by one of us with Bogdanova and Shcheglova [9], who showed for a series of experiments that true activation energies of dehydrogenation of alcohols differ but slightly from the apparent ones and that the difference often lies almost within the experimental error. In the work done by one of us with Isaguliants [10] on dehydrogenation of hydroaromatic hydrocarbons over chromium oxide it was also shown that the difference between the true and the apparent activation energies is not great. This circumstance allows one to use the apparent activation energies for the calculation of the bond energies.

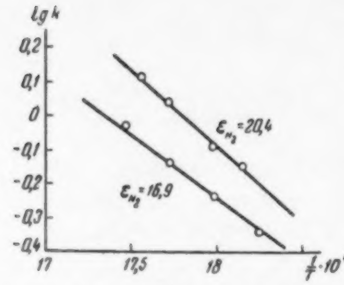

Fig. 5. True activation energies of dehydrogenation of isopropyl alcohol at various activities.

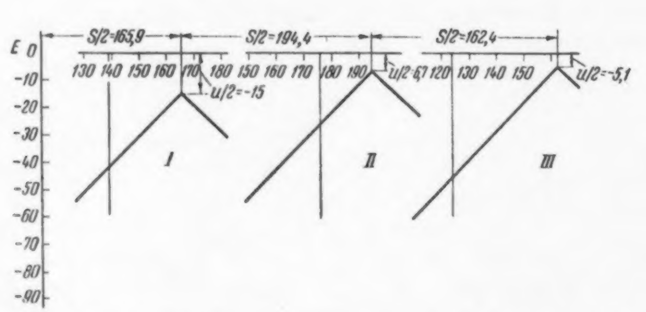

Fig. 6. Volcano-like curves. Dehydrogenation of cyclohexane I; dehydrogenation of isopropyl alcohol II; dehydration of isopropyl alcohol III.

Determination of bond energies. For calculation of the bond energies we used the values, found by us, for apparent activation energies of three reactions: dehydrogenation of cyclohexane (ϵ_{H_2} = 31.4 kilocal/mole), dehydrogenation of isopropyl alcohol (ϵ_{H_2} = 19.2 kilocal/mole) and dehydration of isopropyl alcohol (ϵ_{H_2O} = = 33.0 kilocal/mole). The values of the energy barriers were calculated from the formula: $E = -(4/3)\epsilon$; it was found that E_1 = −41.8 kilocal/mole; E_2 = −25.6 kilocal/mole; E_3 = −44 kilocal/mole. The bond energies were calculated from Formulas (8) from paper [1]; the energies of bonds between atoms of the reacting molecule were taken from Cottrell's monograph [11]. The following values were obtained: Q_{HCr} = 60.8 kilocal; Q_{CCr} = 8.8 kilocal; Q_{OCr} = 45.2 kilocal. The values of the adsorptional potentials turned out to be as follows: q_1 = 139.2 kilocal (dehydrogenation of cyclohexane); q_2' = 175.6 kilocal (dehydrogenation of alcohol); q_3 = 123.6 kilocal (dehydration of the alcohol).

DISCUSSION OF RESULTS

The data obtained by us on the bond energies are compared, in Table 9, with the data taken from Table 1

TABLE 4

Dehydrogenation of Isopropyl Alcohol in the Presence of Hydrogen ($A_1 + A_2$ = 5.89 ml/min · 3 ml catalyst; catalyst volume,10 ml; catalyst,Cr_2O_3)

Temperature in °C					
275		291		299	
alcohol content, mole %	m_{H_2} ml/min	alcohol content, mole %	m_{H_2} ml/min	alcohol content, mole %	m_{H_2} ml/min
100	4,1	100	6,0	100	7,6
82,0	4,2	81,5	5,8	79,3	7,5
47,9	4,1	37,0	5,5	48,8	7,8
				41,9	7,9

TABLE 5

Dehydrogenation of Isopropyl Alcohol in the Presence of Acetone (catalyst Cr_2O_3; catalyst volume 10 ml; $A_1 + A_2$ = 5.89 ml/min · ml cat)

amount of alcohol in mole %	Temperature in °C											
	275			283			291			299		
	v_{gas}, ml/min	m_{H_2}, ml/min	z_2	v_{gas}, ml/min	m_{H_2}, ml/min	z_2	v_{gas}, ml/min	m_{H_2}, ml/min	z_2	v_{gas}, ml/min	m_{H_2}, ml/min	z_2
100	5.00	4.03	—	6.20	4.80	—	8.20	6.00	—	10.6	7.60	—
74.14	2.03	1.72	3.82	3.40	2.35	2.97	3.74	2.91	3.03	5.2	4.10	2.42
65.50	—	—	—	2.70	2.25	2.14	2.60	2.10	3.50	4.7	3.70	2.00
48.87	0.8	0.7	4.56	1.33	1.15	3.04	1.81	1.50	2.88	2.35	1.90	2.88
32.06	—	—	—	—	—	—	0.90	0.80	3.06	1.40	1.21	2.48

TABLE 6

Determination of True Activation Energy of Dehydrogenation of Isopropyl Alcohol catalyst Cr_2O_3 (new activity); ϵ_{true} = 16,900 cal/mole)

Temperature in °C	z_2 from Equations (3) and (4)	k, calc. from Equations (3) and (4)	k, calculated by Equation (5)	log k_0	$\frac{\epsilon_{true}}{\log k_0} \cdot 10^{-3}$	k, calculated from ϵ_{true} = 16,900
275	4.25	0.44	0.46	6.39	2.65	0.45
283	3.40	0.56	0.55	6.39	2.65	0.56
291	3.50	0.69	0.72	6.32	2.67	0.68
299	3.12	0.93	0.92	6.51	2.60	0.87

Average $\log k_0 = 6.40$; $k_0 = 2.51 \cdot 10^6$; $\frac{\epsilon_{true}}{\log k_0} \cdot 10^{-3} = 2.64$

of paper [2]. All bond energies given in Table 9 were determined from the same reactions: dehydrogenation of cyclohexane or methylcyclohexane, and dehydrogenation and dehydration of isopropyl alcohol. It was pointed

TABLE 7

Isopropyl Alcohol—Acetone
(ΔH = 1750 cal/mole)

Temperature °K	z_2	$-\Delta F$ in cal/mole	ΔS in cal/deg mole
548	4.25	1575	6.06
556	3.40	1350	5.57
564	3.50	1400	5.60
572	3.12	1520	4.86

TABLE 8

Determination of True Activation Energy of Dehydrogenation of Isopropyl Alcohol (catalyst Cr_2O_3 (original activity); ϵ_{true} = 20,400 cal/mole)

Temperature in °C	k	$\log k_0$	$\frac{\epsilon_{true}}{\log k_0} \cdot 10^{-3}$	k, calculated from ϵ_{true} = 20,400
278	0.71	7.92	2.57	0.72
283	0.82	7.91	2.58	0.85
291	1.10	7.94	2.57	1.10
296	1.28	7.95	2.56	1.23

Average $\overline{\log k_0}$ = 7.93; $k_0 = 8.51 \cdot 10^7$; $\frac{\epsilon_{true}}{\log k_0} \cdot 10^{-3} = 2.57$.

TABLE 9

Effect of Support on Bond Energy

Catalyst	Q_{HCr}	Q_{CCr}	Q_{OCr}
Cr_2O_3 from $(NH_4)_2Cr_2O_7$	60.8	8.8	45.2
Cr_2O_3 from $(NH_4)_2Cr_2O_7$ on asbestos	57.7	14.8	35.1
Cr_2O_3 from $Cr(NO_3)_3$, precipitated by soda	54.7	11.0	71.8
Cr_2O_3 from $Cr(NO_3)_3$, precipitated by soda on asbestos	60.7	11.9	44.9

in paper [3] that introduction of asbestos leads to a considerable drop of Q_{OCr}. This rule is confirmed by comparison of our data with those obtained on chromium oxide, prepared from ammonium bichromate and deposited on asbestos [12]. It was also pointed out in paper [2] that the catalysts prepared by heating the bichromate yield less strong bonds with oxygen than are formed by the precipitated catalysts. The comparison was made with the catalyst on asbestos, i.e., the second and the third lines in Table 9 were compared. The data from the present work confirmed this regularity as well. However it should be noted that catalysts prepared by heating of the bichromate are also less firmly bonded with carbon. It is true that the deposition of such a catalyst on asbestos leads to a significant increase of Q_{CCr}. A comparison of the locations of the sections on the volcano-like curves (Fig. 6) and Fig. 7 of paper [3] makes it necessary to prefer the catalysts prepared by precipitation.

SUMMARY

1. The kinetics of dehydrogenation and dehydration of isopropyl alcohol on chromium oxide, prepared by heating ammonium bichromate, were studied. The relative adsorptional coefficients of acetone and hydrogen were determined.

2. Activation energies were determined for the following reactions: dehydrogenation and dehydration of isopropyl alcohol and dehydrogenation of cyclohexane.

3. Bond energies of the reacting atoms in the molecule with the catalyst were determined. A comparison was made with the catalytic properties of chromium oxide prepared by other methods.

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REACTIONS OF FREE ETHYL RADICALS WITH MOLECULAR OXYGEN

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The study of the reactions of free aliphatic radicals, and specifically reactions of the ethyl radicals, with molecular oxygen, gains a special significance in connection with the development of the theory of oxidation of hydrocarbons.

A large number of papers are found in the literature in which the reactions of aliphatic radicals with oxygen are used for the design of the mechanism schemes for oxidation of hydrocarbons, without a sufficient foundation, in our opinion. Papers directly devoted to the study of the reactions of radicals with oxygen are few in number.

The papers by Jones and Bates [1], Nalbandian [2], Gray [3], Finkelstein and Noyes [4] are devoted to the study of the reaction of ethyl radicals with molecular oxygen. An analysis of these literature data shows that different viewpoints exist concerning the mechanism of interaction of ethyl radicals with molecular oxygen. Thus, for example, in Nalbandian's paper [2] a conclusion is made that the peroxide radical C_2H_5OO is formed after further transformation of the peroxide. Finkelstein and Noyes [4] consider that the originally formed C_2H_5OO radicals may decompose further by the scheme:

$$
\begin{array}{lll}
 & \nearrow & CH_3CHO + OH \\
C_2H_5O_2 & & \\
 & \searrow & CH_3CO + H_2O \\
 & & \ \downarrow \\
 & & CH_3 + CO
\end{array}
$$

The common defect of the work of previous authors is the impossibility of the solution of the problem of the consecutive nature of formation of the reaction products. For example, it is impossible to decide singularly how acetaldehyde is formed: whether directly from the C_2H_5 radical and O_2, or through a preliminary formation of ethyl hydroperoxide. We note that generally in all photochemical experiments in which the oxygen–hydrocarbon mixture is subjected to illumination, the reaction products are evidently the result of many complex processes. Therefore, the results of such experiments may lead to erroneous interpretations.

In order to avoid the deficiencies in the work of previous authors on the problems connected with the study of reactions of ethyl radicals with molecular oxygen, we selected another path for the solution of this problem, its difference consisting mainly in the possibility of capture of the primary reaction products of the ethyl radical and the oxygen molecule. In addition, we are able to capture the secondary reaction products and distinguish them from the primary reaction products by a method of separation based on the consecutive nature of elementary reactions of radicals and atoms [5]. The ethyl radicals for our experiments were obtained by the action of hydrogen atoms on ethylene. It is significant to note here that the zone of formation of the radical was separated from the zone of its reaction with oxygen and, thus, the interaction and the effect of other factors (light, excited particles, sensitization) were excluded.

EXPERIMENTAL

The experiments were run in a vacuum flow setup made of molybdenum glass. The principal scheme of the apparatus was given by us earlier [5]. Molecular hydrogen (dried previously) passed into the discharge tube supplied by a high tension transformer (5000 volts, 250 ma current strength). Then the stream passed through a nozzle and the reaction vessel. The nozzle had the length of 30 mm and a diameter of 1-1.5 mm at the discharge tube and 3-4 mm at the reaction vessel. Ethylene was supplied to the nozzle and to the reaction vessel through a separate inlet. The temperature was measured with a thermocouple which could be placed in various sites within the reaction vessel. Molecular oxygen was supplied through special inlets to various locations within the reaction vessel. During this, it was necessary to maintain conditions under which the absence of diffusion of oxygen and ethylene into the discharge could be guaranteed. The reaction products were condensed in a removable trap, cooled by liquid nitrogen. A definite volume of water was preliminarily placed in this trap.

The pressure inside the reaction vessel was measured with a mercury manometer with the aid of a measuring microscope. The metering of all the gases was done with a calibrated bulb and stopcock valves. Pumping-down was done with a fore-vacuum pump and a vacuum pump (vacuum pumps had the capacity of 100 liters/sec). The distance between the nozzle and the trap was 40 cm.

The analysis of the products was done as follows: the hydroperoxide was estimated by the polarographic method in 0.02 N HCl solution, as well as by titration of the liberated iodine from the reaction with potassium iodide in acid medium. The aldehydes were determined by the polarographic method in 0.1 N lithium hydroxide solution. Ethylene oxide was estimated by its reaction with a saturated manganous chloride solution. In this reaction the insoluble manganese hydroxide is formed, which was observed in respect to turbidity produced by it. The amount of turbidity was determined with a nephelometer after three days following the mixing of the solutions. In order that it would be possible to determine the concentration of ethylene oxide from this turbidity by means of the nephelometer, the apparatus was first calibrated by various concentrations of ethylene oxide.

Proof of Formation of Ethyl Radicals in the Reaction of Hydrogen Atoms with Ethylene Molecule

It is known [6, 7] that the lead mirror reacts readily with aliphatic radicals and is not touched by hydrogen atoms. It is also known that [8] hydrogen atoms readily react with lampblack. Therefore by placing a lead mirror into the reaction vessel in the path of the stream and by observing the disappearance of the former, it is possible to judge the presence of ethyl radicals in the given site within the vessel. By placing a lampblack "mirror" in the same location in the vessel and by observing its disappearance it is possible to draw conclusions about the existence of hydrogen atoms at that location in the vessel. For the proof of formation of ethyl radicals in the reaction of hydrogen atoms with ethylene under the conditions of our experiments, we ran some experiments with two types of mirrors – lampblack and lead. The lampblack "mirror" was a glass spatula blackened on one side with soot. The lead mirror was a similar spatula onto one side of which a layer of lead had been deposited by vacuum sputtering. The preparation of lead and other metallic mirrors was done in a special apparatus, shown schematically in Fig. 1.

The apparatus was made of quartz glass. Lead was placed into the cavity in the apparatus and was heated, after pumping-down, with a gas burner. The lead vapors were condensed on the surface of the spatula on that side which faced the lead. The opposite side of the spatula was so located by the turn of the joint that it touched the cool surface of cavity 2 and remained clean. It was possible to deposit mirrors of any thickness by this method after sufficient experience. The resulting mirror was then introduced through the joints into the reaction vessel and was placed with its mirror surface being perpendicular to the direction of the flow. Both lead and lampblack mirrors could be located at various distances from the nozzle, depending on which sidearm was used to introduce them into the vessel. We showed that hydrogen atoms, drawn from the discharge in dry hydrogen, removed rapidly (in 5-6 min) the lampblack mirror located 2 cm away from the nozzle. The lead mirror located at the same distance was not affected by hydrogen atoms (in 30 min period) but was rapidly removed (in 1-2 min) by aliphatic radicals which formed after addition of ethylene into the reaction zone. Consequently, the ethyl radical is, indeed, formed in the reaction of a hydrogen atom with ethylene. The conceivable formation of the methyl radical and the coexistence of ethyl and methyl radicals under the conditions of our experi-

ments do not interfere with the study of the reaction of ethyl radicals with molecular oxygen since the reaction products of these radicals would be different. For the study of the reactions of the ethyl radical with a molecule of oxygen, it is important to exclude the reaction of hydrogen atoms since their reaction with the oxygen molecule could lead to formation of oxygen atoms. Therefore, in the study of reactions of the ethyl radical, formed by interaction of $H + C_2H_4$ it is necessary to introduce molecular oxygen into the reaction zone at such distances from the site of mixing of $H + C_2H_4$ at which the hydrogen atoms are absent. Under the conditions of our experiments this distance was 2 cm or more measured from the nozzle.

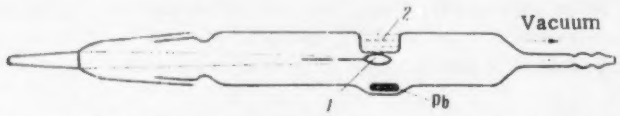


Fig. 1. The scheme of the apparatus for deposition of metallic mirrors under vacuum:
1) glass spatula; 2) cavity.

DISCUSSION OF RESULTS

We have established as a result of these experiments that ethyl radical in reacting with the oxygen molecule forms acetaldehyde, ethylene oxide and a hydroperoxide as the reaction products. It appeared also that the direction of the reaction $C_2H_5 + O_2$ depends on the method of treatment of the surface of the reaction vessel. Formation of ethylene oxide occurs with participation of the surface treated with the products of discharge in water vapor. The surface of the vessel treated with the products from a discharge in hydrogen alters the direction of this reaction so that ethylene oxide is not formed in noticeable amounts. At the same time it appears that this treatment of the vessel surface does not exert any influence on the formation of acetaldehyde.

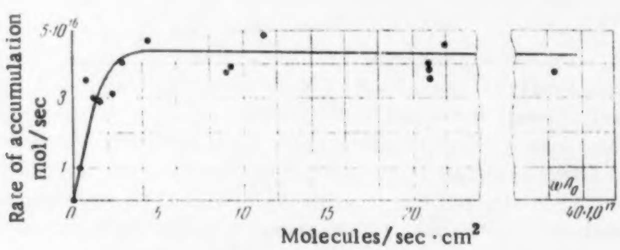


Fig. 2. Dependence of the rate of accumulation of ethylene oxide on the rate of supply of ethylene.

It is characteristic that in no case did we detect any formaldehyde in the reaction of the ethyl radical with an oxygen molecule. Formaldehyde is detected among the reaction products only in case a hydrogen atom appears in the reaction zone, this atom being able to furnish an oxygen atom by reacting with O_2. Thus, for example, formation of formaldehyde was observed in our experiments in those cases in which molecular oxygen was supplied at the site of mixing of H with C_2H_4.

The results of experiments at 220°, obtained in the apparatus whose reaction vessel had the cross-sectional area of $S = 2.31$ cm^2, are given in the table. In these experiments the molecular oxygen was supplied at the distance of 2 cm from the site of mixing of H with C_2H_4. Increased concentration of O_2 in the reaction zone leads, as it is evident in the table, to increased rates of formation of the reaction products. In the case in which the vessel surface had been treated with products from the discharge in water vapors, the main reaction product was ethylene oxide.

Acetaldehyde and the organic hydroperoxide are formed in approximately equal amounts. In the case in which the walls had been treated with the products from the discharge in hydrogen, no ethylene oxide was

TABLE

No. of expt.	Condition of the surface	Total pressure in mm	Velocity of the stream in cm/sec	Rate of supply of ethylene through 1 $cm^2 \cdot 10^{-18}$	Pressure of O_2 in mm	Distance of trap cooled with liquid nitrogen, in cm	Rate of formation of		
							ethylene oxide	acetaldehyde	peroxide
70	Treated with gases from a discharge in water vapors	6	1100	2.5	0.1	40	–	1.64	1.5
87	same	7	1100	3.3	0.04	40	5.4	0.8	1.1
86	"	7	1100	3.3	0.035	40	4.7	0.63	–
93	"	7	1100	3.3	0.015	40	3.5	0.49	–
91	"	7	1100	3.3	0.005	40	3.7	0.43	–
95	"	7	1100	3.3	0.001	40	2.9	0.01	–
98	"	7	1100	3.3	0	40	0	0	0
120	Treated with products of discharge in hydrogen H_2	5	900	4.3	0.025	40	not detected	0.44	–
121	same	5	900	4.1	0.03	150	not detected	0.25	–

detected by our analytical method. Acetaldehyde was formed in practically the same amounts as in the first case. This indicates that the formation of ethylene oxide depends on the condition of the surface of the reaction vessel. In the case in which ethylene oxide is formed in large amounts, the state of the cold wall is without effect on the rate of accumulation of the oxide. As to the presence of carbon dioxide among the reaction products, we failed to detect it by absorption in alkali, owing to the small amount. However it is impossible to say, on this basis alone, that carbon dioxide is not formed, since we measured the content of carbon dioxide in the gas with the accuracy of but 0.4-0.5%. A search for carbon monoxide among the reaction products, under the conditions of our experiments, ended in failure. We could not detect any carbon monoxide,possibly owing to the low sensitivity of the analytical method. Therefore, we are able to say only that if carbon monoxide is formed, its amount does not exceed 25% of the amount of ethylene oxide.

The results of another series of experiments, run in a different vessel, treated with products of a discharge in water vapors, are given in Figs. 2 and 3. Ethyl radicals were prepared in this series of experiments from ethylene and hydrogen atoms, while molecular oxygen was fed directly into the nozzle. Since oxygen was supplied at the site of mixing of H with C_2H_4, the reaction $H + O_2$ was not completely excluded, which evidently led to formation of CH_2O. The experiments were run at temperature $T = 110°$, pressure $p_{H_2} = 8$ mm with addition of oxygen p_{O_2} of about 0.1 mm. The reaction vessel had the cross-sectional area $S = 7.55$ cm^2. As it is evident in Figs. 2 and 3, these experiments measured the rates of accumulation of ethylene oxide, formaldehyde and acetaldehyde, as these were related to the rate of supply of ethylene (wA_0).

In Fig. 4 we show the dependence of the rate of accumulation of ethylene oxide on the concentration of molecular oxygen. As it follows from Fig. 4, the dependence of the rate of accumulation of ethylene oxide, at the constant value of $wA_0 = 21.10^{17}$ molecules/sec$\cdot cm^2$, on the concentration of oxygen in this vessel was approximately the same as already given in the table.

In Fig. 5 we give the results of experiments run in the same vessel at constant value of $wA_0 = 1.9 \cdot 10^{17}$ molecules/sec$\cdot cm^2$, with the vessel having been somewhat treated with hydrogen atoms. Under the definition of "somewhat treated with hydrogen atoms" one should take the fact that in this vessel we ran continuously some experiments using the discharge in hydrogen and that no treatment with products from the discharge in water vapors was performed between the experiments. It appeared that if ethylene oxide is formed in the new vessel, which was still untreated, this substance ceases to be formed during the course of work with a discharge in hydrogen,if the vessel is not treated with the products from a discharge in water vapors.

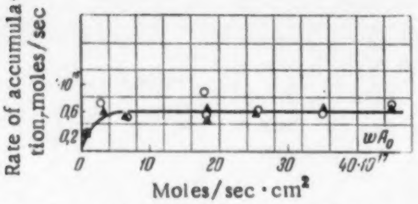


Fig. 3. Dependence of the rates of accumulation of aldehydes on the rate of supply of ethylene:
▲) CH_2O; ○) acetaldehyde.

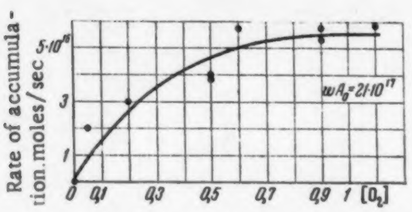


Fig. 4. Dependence of the rate of accumulation of ethylene oxide on oxygen concentration.

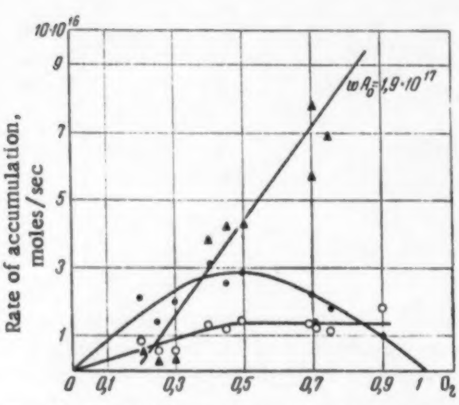


Fig. 5. Dependence of the rate of accumulation of reaction products on the concentration of oxygen in the vessel, pretreated with hydrogen atoms:
▲) formaldehyde; ○) acetaldehyde; ●) ethylene oxide.

It is evident from Fig. 5 that relatively large yields of formaldehyde and, conversely, low yields of ethylene oxide are obtained at sufficiently high concentrations of oxygen. An optimum oxygen concentration exists under these conditions for the formation of ethylene oxide. It is possible to attain the condition under which ethylene oxide would not be formed at any concentration of oxygen, by more extended treatment of the vessel with hydrogen atoms. As to acetaldehyde, its behavior differs from that of formaldehyde and ethylene oxide.

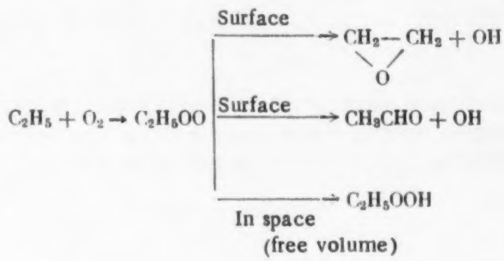
In order to be convinced of the undoubted existence of the process of formation of ethylene oxide from the ethyl radical and an oxygen molecule, we set up some experiments in which the ethyl radical was obtained by another method. The source of ethyl radicals in these experiments was the thermal decomposition of methyl ethyl ketone. An apparatus of quartz glass was made for this purpose. All details, except one, of the molybdenum glass apparatus described previously [5] were retained in this apparatus. In place of the discharge tube, we mounted in the quartz apparatus a platinum spiral which was located opposite the nozzle. Thus, methyl ethyl ketone vapors first passed over the platinum spiral heated to about 800°, then passed into the reaction zone through the nozzle, with molecular oxygen being supplied simultaneously into the reaction zone. Consequently, in these, as well as in our previous experiments, the zone of formation of the radicals was separated from the reaction zone by the nozzle. The vapor pressure of methyl ethyl ketone in the reaction zone of the apparatus did not rise over 0.2 mm without heating of the spiral and rose to 1 mm during such heating. The temperature within the reaction zone did not exceed 100°.

The linear velocity of the stream was about 300 cm/sec. It was shown under these conditions by means of lead mirrors that aliphatic radicals are carried from the nozzle into the reaction zone. A mixture of methyl and ethyl radicals is drawn forth in this case. However, it was necessary for us to be certain of the formation of ethylene oxide from the ethyl radical in the absence of hydrogen atoms. In reality, we found ethylene oxide among the reaction products. Formation of ethylene oxide, from participation of the methyl radicals, is quite improbable and, therefore, the ethylene oxide found by us under these experimental conditions speaks of its formation from the ethyl radical and a molecule of oxygen. A careful search for formaldehyde among the reaction products gave a negative result. Formaldehyde was not detected despite the very sensitive analytical method being used. The latter made use of the reagent: phenylhydrazine hydrochloride solution + test solution + + potassium ferricyanide solution + concentrated hydrochloric acid. It should be noted that in blank experiments, i.e., with decomposition of methyl ethyl ketone under the experimental conditions but without addition of oxygen into the reaction zone, neither ethylene oxide nor formaldehyde were found among the reaction products.

Thus it follows from our experiments that ethylene oxide is formed specifically from the ethyl radical and a molecule of oxygen, but with participation of the specific surface.

We found that ethylene oxide is not formed on walls that had been treated with hydrogen atoms and phosphoric acid. However, it is possible to suppose that we failed to detect any ethylene oxide not because it did not form but because of its being decomposed on the walls of the vessel that had been treated with hydrogen atoms. However, this supposition contradicts the experiment since we did not detect any new oxygen-containing products which should have formed in this case.

Thus, the combination of all the experiments leads us to the conclusion that at temperatures from 100° to 300° the following primary reactions of ethyl radical with an oxygen molecule take place:



SUMMARY

1. Ethylene oxide as well as acetaldehyde and a hydroperoxide are the reaction products of the ethyl radical and molecular oxygen at temperatures from 100° to 300°.

2. The direction of the reaction $C_2H_5 + O_2$ is strongly affected by the state of the surface of the reaction vessel.

3. Formation of ethylene oxide in the reaction of the ethyl radical and a molecule of oxygen occurs on the walls of the reaction vessel that had been treated with the products from a discharge in water vapors.

4. The reaction of the ethyl radical with a molecule of oxygen does not lead to formation of formaldehyde at temperatures up to 300° either by a direct route or through intermediate reactions.

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HOMOLYTIC ISOMERIZATION OF 1,1,1-TRICHLORO-2-BROMOPROPENE

A. N. Nesmeianov, R. Kh. Freidlina and V. N. Kost

The question of the possibility of rearrangement of free radicals in solution remained debatable until recently (see for example [1-3]). A number of such rearrangements have been firmly established at this time. Several cases of rearrangement in radicals, through migration of the aryl group, are known to follow the scheme (1) [4-9]:

$$XC_6H_4\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - \dot{C}H_2 \rightarrow RR'\dot{C} - CH_2C_6H_4X,\ \text{where } R, R' = \text{alkyl, aryl};\ X = H, \text{alkyl}. \qquad (1)$$

Two of the authors of the present paper and Zakharkin [10] found a rearrangement in a radical through migration of chlorine by scheme (2):

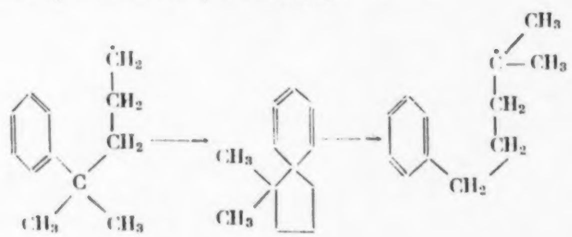
$$CCl_3 - \dot{C}H - CH_2Y \rightarrow \dot{C}Cl_2CHClCH_2Y,\ \text{where } Y = Br, CCl_3 \qquad (2)$$

This rearrangement was observed during the study of the addition reaction of bromotrichloromethane or hydrogen bromide to 1,1,1-trichloropropene in the presence of benzoyl peroxide.

Contradictory data are found in the literature concerning the possibility of rearrangement in radicals through migration of a methyl group. It was shown in a number of papers [9, 11, 12] that the neopentyl radical does not isomerize. Kharasch and co-workers [13] consider that they did observe a rearrangement of this type in bromination of 2,2,4,4-tetramethylpentane at 200° according to scheme (3):

$$(CH_3)_3C - \dot{C}H - C(CH_3)_3 \rightarrow (CH_3)_2\dot{C} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - C(CH_3)_3. \qquad (3)$$

It was shown in several ways [14-17] that rearrangements in radicals through migration of hydrogen from a neighboring carbon atom are impossible; rearrangements through migration of a hydrogen from more remote carbon atoms do take place [14]. A rearrangement occurs during decarbonylation [18] of 5-methyl-5-phenylhexanal, this being represented by the authors by scheme (4):



(4)

As far as it is known to us, not a single case of homolytic transformation of any substance into an isomeric substance has been studied, i.e., a case of a homolytic isomerization is unknown.

In the present paper we report a homolytic isomerization of 1,1,1-trichloro-2-bromopropene into 1,1,2-trichloro-3-bromo-1-propene according to the scheme (5):

$$\underset{(I)}{CCl_3CBr = CH_2} \rightarrow \underset{(II)}{CCl_2 = CCl - CH_2Br}. \qquad (5)$$

A sample of this compound on standing after a certain induction period (over 1-2 days) or under illumination with a mercury lamp for a few minutes, without heating, isomerizes completely into 1,1,2-trichloro-3-bromo-1-propene. Addition of hydroquinone or dimethylaniline to 1,1,1-trichloro-2-bromopropene hinders the isomerization and samples containing the inhibitors were kept for over a month without change.

We suppose that the isomerization proceeds by the following scheme:

$$\begin{aligned}
&a)\ CCl_3CBr = CH_2 \rightarrow Br + C_3H_2Cl_3^{\cdot} \\
&b)\ CCl_3CBr = CH_2 + Br \rightarrow CCl_3\dot{C}BrCH_2Br \\
&c)\ CCl_3\dot{C}Br - CH_2Br \xrightarrow{\text{rearrangement}} \dot{C}Cl_2CClBrCH_2Br \\
&d)\ \dot{C}Cl_2CClBrCH_2Br + CCl_3 - CBr = CH_2 \rightarrow CCl_2 = CClCH_2Br + CCl_3\dot{C}BrCH_2Br.
\end{aligned} \qquad (6)$$

The case of homolytic isomerization of $CCl_3CBr = CH_2$ discovered by us is interesting in that this isomerization differs in direction from the anionotropic allylic rearrangement of the same compound. We showed that 1,1,1-trichloro-2-bromopropene undergoes the allylic rearrangement under the influence of antimony pentachloride or aluminum chloride, forming 1,1,3-trichloro-2-bromo-1-propene. Both rearrangements are compared in scheme (7):

$$\underset{(I)}{CCl_3 - CBr = CH_2} \begin{cases} \xrightarrow{h\nu} \underset{(II)}{CCl_2 = CCl - CH_2Br} \\ \xrightarrow[SbCl_5]{} \underset{(III)}{CCl_2 = CBr - CH_2Cl} \end{cases} \qquad (7)$$

The methods of preparation of the substances under examination and the proof of their structure may be summarized as follows. The starting material for preparation of 1,1,1-trichloro-2-bromopropene was 1,1,1-trichloro-2,3-dibromopropane, formed by the action of bromine on 1,1,1-trichloropropene in acetic acid medium without illumination. 1,1,1-Trichloro-2-bromopropene was obtained by the action of potassium hydroxide in the Ethyl Cellosolve medium on 1,1,1-trichloro-2,3-dibromopropane, with cooling, with the above being the sole reaction product formed by the scheme:

$$CCl_3CHBrCH_2Br \xrightarrow{KOH} CCl_3CBr = CH_2. \qquad (8)$$

The allylic isomer of this compound – 1,1,3-trichloro-2-bromo-1-propene, was formed by scheme (9):

$$CCl_2 = CHCH_2Cl + Br_2 \rightarrow \underset{(IV)}{CCl_2BrCHBrCH_2Cl} \xrightarrow{KOH} \underset{(III)}{CCl_2 = CBrCH_2Cl}. \qquad (9)$$

The structure of substance (IV) was confirmed by hydrolysis with nitric acid (s. g. 1.52) with formation of α-bromo-β-chloropropionic acid in good yield. The latter yielded α-bromoacrylic acid under the influence of alcoholic alkali. See [19] about the action of concentrated nitric acid on polychloroalkanes. Isomerization

of substance (I) into substance (III) under influence of antimony pentachloride [scheme (7)] confirms the structure of (I) since the reverse isomerization of substances of type (III) into substances of type (I) is unknown.

1,1,2-Trichloro-3-bromo-1-propene – the product of homolytic isomerization of substance (I) (scheme 5) – was synthesized by an independent route according to scheme (10):

$$CCl_2 = CClCH_2Cl \xrightarrow[(CH_3)_2CO]{NaBr} \underset{(II)}{CCl_2 = CClCH_2Br}. \tag{10}$$

All three trichlorobromopropene (I) – (III), prepared both by the isomerization by scheme (7) and by the independent route by schemes (9) and (10), were identified in the form of solid hydrochlorides of their diethylamino derivatives, formed by schemes (11) and (12):

$$\underset{(I)}{CCl_3CBr} = CH_2 + (C_2H_5)_2NH \rightarrow \underset{(V)}{CCl_2 = CBrCH_2N(C_2H_5)_2HCl} \tag{11}$$

$$CCl_2 = CBr - CH_2Cl + (C_2H_5)_2NH \nearrow$$

$$\underset{(II)}{CCl_2 = CCl - CH_2Br} + 2(C_2H_5)_2NH \rightarrow$$

$$\rightarrow CCl_2 = CClCH_2N(C_2H_5)_2 \xrightarrow{HCl} \underset{(VI)}{CCl_2 = CClCH_2N(C_2H_5)_2 \cdot HCl} \tag{12}$$

Hydrochloride (VI) did not give a melting point depression on being mixed with an authentic sample prepared previously [20]. 1,1,1-Trichloro-2-bromopropene (I) and its allylic isomer (III), prepared both by isomerization and by scheme (9), yielded the same compound with structure $C_6H_5CH_2CBr = CCl_2$ on reacting with benzene in the presence of aluminum chloride.

EXPERIMENTAL

1,1,1-Trichloro-2-bromopropene.

A solution of 10 g of potassium hydroxide in 75 ml of Ethyl Cellosolve was added dropwise with cooling and stirring to 48 g of 1,1,1-trichloro-2,3-dibromopropane.* Stirring was continued for three hours longer. The oil which separated after dilution with water was removed, washed with water and dried over sodium sulfate. 25 g (71% of theoretical) of 1,1,1-trichloro-2-bromopropene with b. p. 57-58° (15 mm), $n^{20}D$ 1.5323, d^{20}_4 1.8493, was obtained after distillation; found MR* 37.52, calculated MR 37.95.

Nine g (77% of theoretical) of $CCl_2 = CBrCH_2N(C_2H_5)_2$ with b. p. 59° (1 mm), $n^{20}D$ 1.5079, d^{20}_4 1.4060, was obtained by heating 10 g of the trichlorobromopropene with 8.5 g of diethylamine in 50 ml of methylalcohol on a water bath for four hours; found MR 55.33, calculated MR 55.50.

Found %: C 32.35, 35.39; H 4.78, 4.81; N 5.43, 5.26. $C_7H_{12}Cl_2BrN$. Calculated %: C 32.21; H 4.43; N 5.36.

Hydrochloride: m. p. 144-145° (from benzene + chloroform)

Found %: C 28.64, 28.58; H 4.65, 4.58. $C_7H_{13}Cl_3BrN$. Calculated %: C 28.26; H 4.45.

Fourteen g (78% of theoretical) of $C_6H_5CH_2CBr = CCl_2$ with b. p. 97-98° (2 mm), $n^{20}D$ 1.5840, d^{20}_4 1.5566, was obtained by heating 15 g of 1,1,1-trichloro-2-bromopropene with 50 ml of benzene in the presence of 0.5 g of aluminum chloride; found MR 57.19, calculated MR 57.19.

Found %: C 40.80, 40.93; H 2.56, 2.64. $C_9H_7Cl_2Br$. Calculated %: C 40.64; H 2.65.

Isomerization of 1,1,1-Trichloro-2-bromopropene

a) Allylic rearrangement in the presence of $SbCl_5$. 0.2 ml of $SbCl_5$ was added with cooling to 10 g of

* 1,1,1-Trichloro-2,3-dibromopropane was prepared by the action of bromine on 1,1,1-trichloropropene in acetic acid; for more detail of bromination of 1,1,1-trichloropropene see [21].

* Molecular refraction.

1,1,1-trichloro-2-bromopropene. After two hours' standing at room temperature, the reaction mixture was washed with dilute hydrochloric acid, then with water, and was dried over calcium chloride. 7.5 g of 1,1,3-trichloro-2 bromo-1-propene with b. p. 81-82° (21 mm), $n^{20}D$ 1.5522, $d^{20}{}_4$ 1.8954, was obtained after a distillation; found MR 37.83; calculated MR 37.95; the product was identical in all respects with the trichlorobromopropene prepared by dehydrobromination of $CCl_2BrCHBrCH_2Cl$ (see below).

1,1,1-Trichloro-2-bromo-1-propene yields 1,1-dichloro-2-bromo-3-phenyl-1- propene with b. p. 97-98° (2 mm), $n^{20}D$ 1.5840, $d^{20}{}_4$ 1.5566, in good yield by reaction with benzene in the presence of aluminum chloride and the product is identical with dichlorobromophenylpropene prepared by the condensation of 1,1,1-trichloro-2-bromopropene with benzene (see above). By a reaction with diethylamine in methyl alcohol solution we prepared $CCl_2 = CBrCH_2N(C_2H_5)_2$ with b. p. 61-62° (1.5 mm), $n^{20}D$ 1.5085, $d^{20}{}_4$ 1.4068. Hydrochloride: m. p. 144-145°. Mixed melting point with the hydrochloride sample prepared by the action of diethylamine on 1,1,1-trichloro-2-bromopropene (see above) and by the following scheme:

$$CCl_2BrCHBr - CH_2Cl \xrightarrow{KOH} CCl_2 = CBr - CH_2Cl \xrightarrow{HN(C_2H_5)_2} CCl_2CBrCH_2N(C_2H_5)_2 \cdot HCl$$

(see below) showed no depression.

b) Homolytic isomerization. 1,1,1-Trichloro-2-bromopropene isomerized completely into 1,1,2-trichloro-3-bromo-1-propene with b. p. 78-79° (19 mm), $n^{20}D$ 1.5550, $d^{20}{}_4$ 1.8835, after standing following a certain induction period; found MR 38.23, calculated MR 37.95.

Found %: C 15.80, 15.72; H 0.85, 0.82. $C_3H_2Cl_3Br$. Calculated %: C 16.06; H 0.89.

The same isomerization occurs under illumination of 1,1,1-trichloro-2-bromopropene with a mercury lamp. The isomerization is blocked by addition of small amounts of hydroquinone or dimethylaniline to the trichlorobromopropene. Thus, samples with addition of hydroquinone or dimethylaniline were preserved for over a month without change, while complete isomerization occurred in 1-2 days without addition of these substances.

The structure of 1,1,2-trichloro-3-bromopropene was confirmed by the preparation of 1,1,2-trichloro-3-diethylamino-1-propene with b. p. 68° (2.5 mm), $n^{20}D$ 1.4885, $d^{20}{}_4$ 1.1910, by the action of diethylamine on the former. Literature data [20]: b. p. 72° (3 mm), $n^{20}D$ 1.4888, $d^{20}{}_4$ 1.1922. A mixed melting point of the hydrochloride of this amine with the hydrochloride of an authentic 1,1,2-trichloro-3-diethylamino-1-propene gave no depression.

1,1,2-Trichloro-3-bromo-1-propene was also prepared by the action of sodium bromide in acetone on 1,1,2,3-tetrachloro-1-propene and the product had the following constants: b. p. 79-80° (20 mm), $n^{20}D$ 1.5550, $d^{20}{}_4$ 1.8820.

1,1,3-Trichloro-1,2-dibromopropane.

A solution of 48 g of bromine in 50 ml of chloroform was gradually added to a solution of 43 g of 1,1,3-trichloro-1-propene in 50 ml of chloroform. The chloroform was distilled off after completion of the reaction and the residue was vacuum distilled. There was obtained 85 g (94% of theoretical) of 1,1,3-trichloro-1,2-dibromopropane with b. p. 66-67° (1 mm), $n^{20}D$ 1.5678, $d^{20}{}_4$ 2.1874; found MR 45.64, calculated MR 46.18.

Found %: C 11.71, 11.60; H 0.98, 0.96. $C_3H_3Cl_3Br_2$. Calculated %: C 11.80; H 0.99.

A solution of 15 g of trichlorodibromopropane in 30 ml of nitric acid (s. g. 1.52) was heated carefully, at first, until the violent reaction ceased, after which it was refluxed for 0.5 hour. After dilution with water, the mixture was repeatedly extracted with chloroform. The chloroform extracts were washed with a soda solution to separate the acidic products. After acidification of the soda solution, the precipitated acid was extracted with chloroform and the extract was dried with calcium chloride. 7.2 g (76% of theoretical) of α-bromo-β-chloropropionic acid with b. p. 125-126° (15 mm), m. p. 43-44°, was obtained after a distillation. Literature data [22]: m. p. 43°. α-Bromoacrylic acid with m. p. 69° was obtained by the action of an alcoholic solution of potassium hydroxide on this substance.

1,1,3-Trichloro-2-bromo-1-propene

The dehydrobromination of 1,1,3-trichloro-1,2-dibromopropane was run similarly to the dehydrobromina-

tion reaction of 1,1,1-trichloro-2,3-dibromopropane. Thereupon from 70 g of 1,1,3-trichloro-1,2-dibromopropane we obtained 22 g of 1,1,3-trichloro-2-bromo-1-propene with b. p. 81-82° (21 mm), $n^{20}D$ 1.5522, d^{20}_4 1.8955, after a distillation of the reaction product through a column; found MR 37.83, calculated MR 37.95.

Found %: C 15.82, 16.00; H 0.88, 0.77. $C_3H_2Cl_3Br$. Calculated %: C 16.06; H 0.89.

In addition, we also obtained 13 g of dichlorodibromopropene with b. p. 97-98° (21 mm), $n^{20}D$ 1.5845, d^{20}_4 2.1957; found MR 41.00, calculated MR for $C_3H_2Cl_2Br_2$ 40.85.

Found %: C 13.28, 13.40; H 0.73, 0.75. $C_3H_2Cl_2Br_2$. Calculated %: C 13.40; H 0.75.

1,1-Dichloro-2-bromo-3-diethylamino-1-propene with b. p. 65-66° (1 mm), $n^{20}D$ 1.5079, d^{20}_4 1.4060. was obtained by the action of diethylamine in methyl alcohol solution on either the trichlorobromopropene obtained above or on dichlorodibromopropene; found MR 55.33, calculated MR 55.50. Hydrochloride – m. p. 144-145° (from benzene + chloroform).

SUMMARY

1,1,1-Trichloro-2-bromopropene isomerizes by a homolytic route under the action of ultraviolet light and forms 1,1,2-trichloro-3-bromopropene as well as by the heterolytic route under the action of antimony pentachloride with formation of 1,1,3-trichloro-2-bromopropene.

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BROMINATION OF 1,1,1-TRICHLOROPROPENE

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Two of the authors of this paper and Firstov [1] described the bromination of 1,1,1-trichloropropene. The structure of 1,1,1-trichloro-2,3-dibromopropane was assigned to the trichlorodibromopropane thus formed, on the basis of the usual analogies. Later [2] during a study of the addition of hydrogen bromide and bromotrichloromethane to 1,1,1-trichloropropene in the presence of benzoyl peroxide, a rearrangement was established in the intermediately formed free radical:

$$CCl_3\dot{C}H - CH_2X \rightarrow \dot{C}Cl_2 - CHClCH_2X, \text{ where } X = Br, CCl_3.$$

It was possible to suppose in this connection that the bromination of 1,1,1-trichloropropene may proceed, depending on the reaction conditions, either without a rearrangement (electrophilic addition) or with a rearrangement (homolytic addition):

$$CCl_3CH = CH_2 + \dot{Br} \rightarrow CCl_3CHCH_2Br \rightarrow \dot{C}Cl_2CHClCH_2Br$$
$$\dot{C}Cl_2 - CHClCH_2Br + Br_2 \rightarrow BrCCl_2CHClCH_2Br + \dot{Br}.$$

The clarification of this has a fundamental interest since reactions of addition of bromine to unsaturated compounds are often used for the proof of structure and for identification of unsaturated compounds.

In connection with the above, we undertook a study of the reaction of bromination of 1,1,1-trichloropropene and obtained the following results. In media which aid the heterolytic addition, for example in acetic acid in ether in the presence of hydrogen bromide, the reaction between 1,1,1-trichloropropene and bromine occurs by one path with formation of 1,1,1-trichloro-2,3-dibromopropane. A neutral nitrogenous substance, whose analysis corresponded to a nitrate with the composition $C_3H_3Cl_3BrNO_3$, was obtained by the action of nitric acid (s. g. 1.52) on this substance. 1,1,1-Trichloro-2,3-dibromopropane forms 1,1,1-trichloro-2-bromopropene as the sole dehydrobromination product in the reaction with potassium hydroxide in Ethyl Cellosolve.

A mixture of evidently 1,1,1-trichloro-2,3-dibromopropane and 1,1,2-trichloro-1,3-dibromopropane, which is inseparable by distillation, was formed by running the bromination in chloroform medium under illumination with a 150 watt incandescent lamp. Hydrolysis of this mixture with nitric acid (s. g. 1.52) gave a 20% yield of α-chloro-β-bromopropionic acid. See [3] about the hydrolysis of polyhaloalkanes with concentrated nitric acid. A mixture of bromotrichloropropenes was obtained by the action of potassium hydroxide in Ethyl Cellosolve on this mixture and the products were separated in the form of their diethylamino derivatives:

$$\left.\begin{array}{l} CCl_3CHBrCH_2Br \\ CCl_2BrCHClCH_2Br \end{array}\right\} \xrightarrow{KOH} \left.\begin{array}{l} \rightarrow CCl_3CBr = CH_2 \\ \rightarrow CCl_2BrCCl = CH_2 \end{array}\right\} \xrightarrow{NH(C_2H_5)_2}$$
$$\rightarrow CCl_2 = CBr - CH_2N(C_2H_5)_2 + CCl_2 = CCl - CH_2N(C_2H_5)_2.$$

The proportion of the resulting diethylamino derivatives was:

$27\% \ CCl_2 = CClCH_2N(C_2H_5)_2$ and $73\% \ CCl_2 = CBrCH_2N(C_2H_5)_2$.

Even more 1,1,2-trichloro-1,3-dibromopropane is formed by running the bromination of trichloropropene with bromine in carbon tetrachloride solution with heating in the presence of benzoyl peroxide. The mixture thus resulting of trichlorodibromopropanes yields about 30% of α-chloro-β-bromopropionic acid after hydrolysis with nitric acid. The distillation of diethylamino derivatives, prepared from the trichlorobromopropenes, formed in turn by dehydrobromination of the mixture of trichlorodibromopropanes, gave 70% of $CCl_2 = CCl-CH_2N(C_2H_5)_2$ and only 30% of $CCl_2 = CBrCH_2N(C_2H_5)_2$.

EXPERIMENTAL

Bromination of 1,1,1-trichloropropene in acetic acid. A solution of 24 g of bromine in 30 ml of acetic acid was added in portions to a solution of 21 g of 1,1,1-trichloropropene in 20 ml of acetic acid. The mixture was diluted with water after the completion of the reaction. The resulting dibromide was separated, washed with water, soda solution and again water, and was dried with calcium chloride. 36 g (80% of theoretical) of 1,1,1-trichloro-2,3-dibromopropane with b. p. 69° (2 mm), $n^{20}D$ 1.5630, d^{20}_4 2.1751, was obtained after distillation; found MR 45.58, calculated MR 46.18.

A solution of 15 g of 1,1,1-trichloro-2,3-dibromopropane in 35 ml of nitric acid (s. g. 1.52) was heated to boiling for 20 minutes. Only traces of acidic products were obtained as the result of the reaction, along with 12 g of neutral substance with b. p. 79-80° (2 mm), $n^{20}D$ 1.5240, d^{20}_4 1.9115.

Found %: C 12.63, 12.57; H 1.11, 0.89; N 4.33, 4.44. $C_3H_3Cl_3BrNO_3$. Calculated %: C 12.54; H 1.05; N 4.09.

1,1,1-Trichloro-2-bromopropene was obtained as the sole product from dehydrobromination of 1,1,1-trichloro-2,3-dibromopropane. The properties and the proof of structure of this compound are given in [4].

Bromination of 1,1,1-trichloropropene in chloroform. A solution of 40 g of bromine in 30 ml of chloroform was added in portions to a solution of 36 g of trichloropropene in 25 ml of chloroform with stirring and under illumination with a 150 watt incandescent lamp. After the distillation of the solvent, the residue was vacuum distilled. A constant-boiling mixture of dibromides with structures $CCl_3CHBrCH_2Br$ and $CCl_2BrCHClCH_2Br$; with b. p. 61-62° (1 mm), $n^{20}D$ 1.5637, d^{20}_4 2.1756, was obtained in 65 g yield (85% of theoretical).

A solution of 15 g of this mixture in 35 ml of nitric acid (s. g. 1.52) was carefully heated to boiling for 20 minutes. The reaction products were extracted with chloroform after dilution with water. The chloroform extract was treated with a soda solution. 2 g (21% of theoretical) of α-chloro-β-bromopropionic acid with b. p. 134-136° (21 mm) was isolated by distillation after acidification of the sodium carbonate extracts and extraction. α-Chloroacrylic acid with m. p. 64-65° was obtained in good yield from the latter by the action of alcoholic potassium hydroxide. Literature data [5]: m. p. 65°. The neutral products, amounting to 6.5 g, had b. p. 79-80° (2 mm), $n^{20}D$ 1.5260.

A mixture of trichlorobromopropenes was obtained by dehydrobromination of 48 g of dibromotrichloropropanes with 10 g of potassium hydroxide in 75 ml of Ethyl Cellosolve. Distillation of this mixture gave the following fractions:*

Fraction I, b. p. 48-49° (9 mm), $n^{20}D$ 1.5340, d^{20}_4 1.8517, 19 g.
Fraction II, b. p. 49-60° (9 mm), 6 g.
Residue 7 g.

Fraction I was evidently a mixture of $CCl_3CBr = CH_2$ and $CCl_2BrCCl = CH_2$ since the action of diethylamine in methyl alcohol solution on this fraction gave 3.8 g of pure $CCl_2 = CClCH_2N(C_2H_5)_2$ (b. p. 61-62° (2 mm), $n^{20}D$ 1.4890, d^{20}_4 1.1980). The hydrochloride had m. p. 168-169°. Literature data [6]: b. p. 72° (3 mm), $n^{20}D$ 1.4888, d^{20}_4 1.1922; hydrochloride – m. p. 168-169°. Ten g of $CCl_2 = CBrCH_2N(C_2H_5)_2$ was also obtained (b. p. 68-69° (2 mm), $n^{20}D$ 1.5080, d^{20}_4 1.4060; hydrochloride – m. p. 144°). Literature data [4]: b. p. 59° (1 mm), $n^{20}D$ 1.5079, d^{20}_4 1.4060; hydrochloride – m. p. 144-145°.

*Hydroquinone was added, for stabilization of the trichlorobromopenes during the distillation, both to the distilling flask and to the receivers.

Two g of $CCl_2 = CClCH_2Br$ was isolated from Fraction II; this had b. p. 78-79° (19 mm), $n^{20}D$ 1.5550, d^{20}_4 1.8834. Literature data [4]: b. p. 78-79° (19 mm), $n^{20}D$ 1.5550, d^{20}_4 1.8835.

Bromination of 1,1,1-trichloropropene in carbon tetrachloride, in the presence of benzoyl peroxide. A solution of 48 g of bromine and 0.5 g of benzoyl peroxide in 50 ml of carbon tetrachloride was added dropwise to a boiling solution of 45 g of 1,1,1-trichloropropene in 50 ml of carbon tetrachloride. After distillation of the solvent, the residue was vacuum distilled. Almost the entire reaction product distilled at 75° (3 mm), $n^{20}D$ 1.5640, d^{20}_4 2.1710.

3.5 g of α-chloro-β-bromopropionic acid and 3.8 g of a neutral substance with b. p. 79-80° (2 mm), and $n^{20}D$ 1.5245, were obtained by the action of 35 ml of concentrated nitric acid (s. g. 1.52) on 15 g of the resulting product and the usual treatment.

Sixteen g of trichlorobromopropenes with b. p. 49-50° (10 mm), $n^{20}D$ 1.5380, and 3.5 g of 1,1,2-trichloro--3-bromopropene with b. p. 78-79° (19 mm), $n^{20}D$ 1.5550, d^{20}_4 1.8834, were obtained after dehydrobromination of 45 g of the trichlorodibromopropanes by the above-described technique. The mixture of trichlorobromopropenes with b. p. 49-50° (10 mm) was separated in the form of their diethylamino derivatives. This yielded 7 g of $CCl_2 = CClCH_2N(C_2H_5)_2$ with b. p. 61-62° (2 mm) ($n^{20}D$ 1.4891, d^{20}_4 1.1985; hydrochloride – m. p. 168-169°) and 3 g of $CCl_2 = CBrCH_2N(C_2H_5)_2$ with b. p. 68-69° (2 mm), $n^{20}D$ 1.5080, d^{20}_4 1.4057; hydrochloride – m. p. 144°.

SUMMARY

1. The reaction of bromination of 1,1,1-trichloropropene under various conditions was examined.

2. The reaction proceeds in a single path in strongly polar media and yields the normal addition product – 1,1,1-trichloro-2,3-dibromopropane.

3. 1,1,2-Trichloro-1,3-dibromopropane, whose formation is explained by a homolytic isomerization of the intermediately formed free radical $CCl_3\dot{C}HCH_2Br \rightarrow \dot{C}Cl_2CHClCH_2Br$, is formed along with 1,1,1-trichloro-2,3-dibromopropane if the reaction is run in nonpolar media under illumination or in the presence of benzoyl peroxide.

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STUDIES IN THE FIELD OF DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

21. ESTERS AND AMIDES OF β-ETHYLHEXOXYVINYLPHOSPHONIC ACID

K. N. Anisimov and B. V. Raisbaum

The present work is a link in the chain of studies of phosphonic acids and their derivatives prepared by the reaction of addition of phosphorus pentachloride to unsaturated compounds. The chloride of β-(β-ethylhexoxy)-vinylphosphonic acid was prepared by the previously described method [1] by the action of phosphorus pentachloride on vinyl 2-ethylhexyl ether.

$$\underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2 - OCH = CH_2 + 2PCl_5 \rightarrow \underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2 - OCHCl - CH_2PCl_4PCl_5 +$$

$$\underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2 - OCHCl - CH_2PCl_4PCl_5 + 2SO_2 \rightarrow$$

$$\rightarrow \underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2OCH = CHPOCl_2 + POCl_3 + 2SOCl_2 + HCl.$$

The method of Milobedzki and Sachnowski [2] was used for the preparation of neutral esters of β-(β-ethylhexoxy)-vinylphosphonic acid by the action of the chloride on alcohols in benzene medium.

$$\underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2 - OCH = CHPOCl_2 + 2ROH + 2C_5H_5N \rightarrow \underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2OCH=$$

$$= CHPO(OR)_2 + 2C_5H_5N \cdot HCl.$$

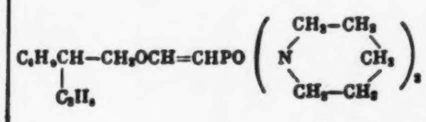
The resulting esters of β-(β-ethylhexoxy)-vinylphosphonic acid were thick, colorless or slightly yellow liquids which were readily soluble in organic solvents. Beginning with the isoamyl ester, these products were distilled under high vacuum,since they decompose during the normal vacuum distillation. In addition, we synthesized the tetramethyldiamide, tetraethyldiamide and the dipiperidide of β-(β-ethylhexoxy)-vinylphosphonic acid by Michaelis' method [3]:

$$\underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2 - OCH = CHPOCl_2 + R_2NH \longrightarrow$$

$$\longrightarrow \underset{\substack{|\\ C_2H_5}}{C_4H_9CH} - CH_2OCH = CHPO[N(R)_2]_2 + 2R_2NH \cdot HCl.$$

The resulting compounds and their physical properties are given in the table (see p. 1166).

Name of substance	Formula of substance	Yield, in % theoretical	B. p. in °C (p in mm of Hg)	n_D^{20}	d_4^{20}	MR calc.	MR found	Found, % C	Found, % H	Found, % P	Calculated, % C	Calculated, % H	Calculated, % P
β-(β-Ethylhexoxy)-vinylphosphonic dichloride	$C_4H_9CH(C_2H_5)-CH_2OCH=CHPOCl_2$	85,5	151—152 (3)	1,4863	1,087	67,61	68,98	44,05 44,10	7,06 7,10	11,22 11,31	43,96	6,95	11,31
Diethyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OC_2H_5)_2$	85,4	143—144 (0)	1,4553	1,0084	78,90	78,62	57,51 57,51	10,24 10,17	10,55 10,53	57,53	9,93	10,62
Dipropyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OC_3H_7)_2$	77	168—170 (2)	1,4530	0,9782	88,13	88,42	59,88 59,80 59,54	10,23 10,24 10,12	9,64 9,34 9,80	60,00	10,31	9,68
Dibutyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OC_4H_9)_2$	69	182—183 (2,5)	1,4540	0,9631	97,27	97,84	62,00 62,17	10,79 10,80	9,01 9,00	62,06	10,63	8,90
Di-isobutyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OC_4H_9\text{-}i)_2$	69	174—175 (0,5)	1,4514	0,9621	97,27	97,46			8,99 9,09			8,90
Di-isoamyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)[O(CH_2)_2-CH(CH_3)_2]_2$	79	Under high vacuum 159 ($10\cdot10^{-4}$)	1,4540	0,9547	106,60	106,65			8,18 8,22			8,24
Dihexyl β-(β-ethylhexoxy)-vinylphosphoate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)[O(CH_2)_5CH_3]_2$	63	Under high vacuum 210 ($10\cdot10^{-4}$)	1,4556	0,9425	115,84	116,43	65,40 65,36	11,29 11,09	7,47 7,47	65,34	11,13	7,67

Name of Substance	Formula of substance	Yield, in % theoretical	B. p. in °C (p in mm of Hg)	n_D^{20}	d_4^{20}	MR		Found in %			Calculated in %		
						calc.	found	C	H	P	C	H	P
Di-β-ethylhexyl β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OCH_2CH(C_2H_5)C_4H_9)_2$	50	Under high vacuum	1,4563	0,9289	134,31	134,69			6,67 6,82			6,73
Di-(methoxyethyl) β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OCH_2CH_2OCH_3)_2$	85	»	1,4578	1,0410	91,41	92,23	54,61 54,62	9,40 9,25	8,45 8,45	54,54	9,37	8,80
Di-(ethoxyethyl) β-(β-ethylhexoxy)-vinylphosphonate	$C_4H_9CH(C_2H_5)-CH_2OCH=CHP(O)(OCH_2CH_2OC_2H_5)_2$	90	»	1,4560	1,0372	100,65	99,59	56,66 56,58	9,69 9,73	7,97 7,74 8,09	56,84	9,37	8,15
N,N,N',N'-Tetramethyl-β-(β-ethylhexoxy)-vinylphosphonodiamide	$C_4H_9CH(C_2H_5)-CH_2-OCH=CHPO[N(CH_3)_2]_2$	79	171—172 (2)	1,4748	0,9831	82,82	83,02			10,69 10,76			10,68
N,N,N',N'-Tetraethyl-β-(β-ethylhexoxy)-vinylphosphonodiamide	$C_4H_9CH(C_2H_5)-CH_2OCH=CHPO[N(C_2H_5)_2]_2$	69	181—182 (2)	1,4720	0,9526	101,29	101,70			8,85 8,78			8,95
β-(β-Ethylhexoxy)-vinylphosphonic dipiperidide		43	Under high vacuum 191 ($2\cdot10^{-2}$)	1,5060	1,0348	106,13	106,23			8,30 8,51			8,37

EXPERIMENTAL

Vinyl 2-ethylhexyl ether was prepared by the method of Favorskii and Shostakovskii [4].

β-(β-Ethylhexoxy)-vinylphosphonic dichloride. The reaction was run in an Erlenmeyer flask provided with a dropping funnel and a calcium chloride tube. 61 g (0.4 mole) of vinyl 2-ethylhexyl ether, diluted with two partsof dry benzene, was added from a dropping funnel gradually with shaking to a suspension of 166.5 g (0.8 mole) of phosphorus pentachloride. A white crystalline precipitate formed with an oily layer above it. The reaction mixture was set aside overnight. A stream of sulfur dioxide was passed into it on the following day until the precipitate disappeared completely as did the oily layer. After the distillation of the solvent, phosphorus oxychloride and thionyl chloride, the residue was subjected to a vacuum distillation. Yield: 78 g (85.5% of theoretical); the constants and the elemental analysis are given in the table.

Diethyl β-(β-ethylhexoxy)-vinylphosphonate. 100-150 ml of dry benzene, 10 g (0.2 mole with slight excess) of absolute ethyl alcohol and 16.8 g (0.2 mole with slight excess) of dry pyridine were placed into a three-necked flask provided with a stirrer, a reflux condenser and a dropping funnel. The condenser and the dropping funnel were protected with calcium chloride tubes. 27.3 g (0.1 mole) of β-(β-ethylhexoxy)-vinylphosphonic dichloride, diluted with an equal volume of benzene, was added dropwise with strong cooling and stirring. After the addition of the chloride, the reaction mixture was heated for two hours on a water bath. Then the precipitate of pyridine hydrochloride was filtered off, the filtrate was washed three times with a 3% soda solution, followed by a water wash after which it was dried over calcined magnesium sulfate. After the distillation of the solvent, the residue was vacuum distilled. Yield: 25 g (85.4% of theoretical) [the constants and the analysis are given in the table]. Dipropyl, dibutyl, di-isobutyl, di-isoamyl, dihexyl, di-2-ethylhexyl, di(methoxyethyl) and diethoxyethyl esters of β-(β-ethylhexoxy)-vinylphosphonic acid were prepared in a similar manner.

N,N,N',N'-Tetramethyl-β-(β-ethylhexoxy)-vinylphosphonodiamide. 100 ml of dry iso-octane and 19 g (0.4 mole with a slight excess) of dry dimethylamine were placed into a three-necked flask, provided with a stirrer, a reflux condenser and a dropping funnel. 27.3 g (0.1 mole) of β-(β-ethylhexoxy)-vinylphosphonic dichloride, diluted with an equal volume of iso—octane, was added dropwise to the mixture, cooled with ice-salt mixture. The mixture was set aside overnight after the addition of the chloride. The precipitate of dimethylamine hydrochloride was filtered off, on the following day after two hours of heating on a water bath, and was washed three times with iso-octane. Then the filtrate was treated with 1% soda solution, was washed with water and dried over dried potassium carbonate. The residue, after the distillation of the solvent, was vacuum distilled. Yield: 23 g (79% of theoretical); the constants and the analysis are given in the table.

The tetraethyldiamide and the dipiperidide of β-(β-ethylhexoxy)-vinylphosphonic acid were prepared in a similar manner.

SUMMARY

β-(β-Ethylhexoxy)-vinylphosphonic dichloride, diethyl, dipropyl, dibutyl, di-isobutyl, di-isoamyl, dihexyl, di-2-ethylhexyl, di-(methoxyethyl) and di(ethoxyethyl) esters of β-(β-ethylhexoxy)-vinylphosphonic acid, tetramethyldiamide, tetraethyldiamide and dipiperidide β-(β-ethylhexoxy)-vinylphosphonic acid were prepared and characterized.

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*See C. B. Translation.

β-ETHYLMERCAPTOETHYL PHOSPHITES AND SOME OF THEIR PROPERTIES

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It was interesting to synthesize and to study the properties of esters of acids of phosphorus containing a hetero-atom in the β-position of the alkyl group, in connection with the studies of tautomerism of organophosphorus compounds. For the first object of this type, we selected the di-(β-ethylmercaptoethyl) hydrogen phosphite (II). We failed to isolate this substance under the conditions of the usual synthesis of dialkyl hydrogen phosphites [1]:

$$PCl_3 + 3ROH \longrightarrow HPO(OR)_2 + RCl + 2HCl$$

the sole isolated product was β-chlorodiethyl sulfide. Later we proposed to prepare di-(β-ethylmercaptoethyl) hydrogen phosphite by cleavage of one alkoxy group from tri-(β-ethylmercaptoethyl) phosphite (I). The latter was synthesized by the action of phosphorus trichloride on β-hydroxydiethyl sulfide in the presence of a tertiary base [2]:

$$3C_2H_5SC_2H_4OH + PCl_3 + 3B \rightarrow 3\ddot{B}\cdot HCl + (C_2H_5SC_2H_4O)_3P, \qquad (I)$$

where $\ddot{B}$ — dimethylaniline, triethylamine or pyridine. However, the cleavage of the neutral ester (I) with a calculated amount of acid led only to a difficulty separable mixture of substances.

We accomplished the synthesis of di-(β-ethylmercaptoethyl) hydrogen phosphite by modification [3] of the above-cited reaction, according to the following equation:

$$\begin{gathered} PCl_3 + 3C_2H_5SC_2H_4OH + 2C_6H_5N(CH_3)_2 \rightarrow 2C_6H_5N(CH_3)_2\cdot HCl + \\ + C_2H_5SC_2H_4Cl + (C_2H_5SC_2H_4O)_2POH \end{gathered} \qquad (II)$$

Here, a mixture of 2 moles of dimethylaniline and 2 moles of β-hydroxydiethyl sulfide was added with cooling to a solution of phosphorus trichloride in benzene, after which the remaining β-hydroxydiethyl sulfide was added. Similar results were obtained also from another variant of the synthesis [4] by the following scheme:

$$\begin{gathered} PCl_3 + 2C_2H_5SC_2H_4OH + 2C_6H_5N(CH_3)_2 \rightarrow (C_2H_5SC_2H_4O)_2PCl + \\ + 2C_6H_5N(CH_3)_2\cdot HCl \xrightarrow{H_2O} (C_2H_5SC_2H_4O)_2POH + HCl. \end{gathered}$$

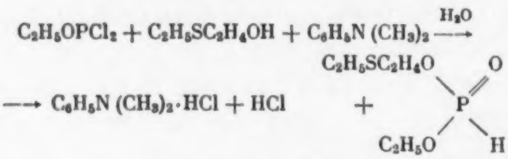
In this case, a mixture of hydroxydiethyl sulfide and dimethylaniline was added to a solution of phosphorus trichloride in benzene. Water was slowly added to the mixture, after the completion of the reaction.

The quite material condition for the isolation of di-(β-ethylmercaptoethyl) hydrogen phosphite is the liberation of the crude reaction product from acidic impurities. If this condition is not fulfilled, the resulting dialkyl hydrogen phosphite cannot be distilled even under high vacuum: either a total decomposition of the substance or its high dispersion occurs: (the corresponding trialkyl phosphite was isolated).

$$2HPO(OC_2H_4SC_2H_5)_2 \rightarrow P(OC_2H_4SC_2H_5)_3 + HPO(OH)(OC_2H_4SC_2H_5)$$

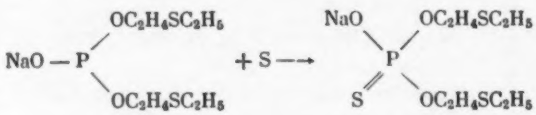
(the corresponding trialkyl phosphite was isolated).

Ethyl β-ethylmercaptoethyl hydrogen phosphite was prepared similarly to di-(β-ethylmercaptoethyl) hydrogen phosphite:



(III)

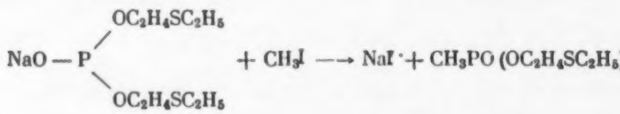
Some properties of the resulting β-ethylmercaptoethyl phosphites were studied. Thus, like the usual dialkyl hydrogen phosphites [5], these substances form sodium derivatives. The sodium salt of di-(β-ethylmercaptoethyl) hydrogen phosphite readily adds sulfur [6]



(IV)

forming the well crystallizable di-(β-ethylmercaptoethyl) sodium thiophosphate.

Sodium di-(β-ethylmercaptoethyl) phosphite also readily reacts in the Michaelis-Becker reaction [7]:



(V)

forming di-(β-ethylmercaptoethyl) methylphosphonate (V). The latter was also synthesized by the Arbuzov reaction from tri-(β-ethylmercaptoethyl) phosphite and methyl iodide:

$$P(OC_2H_4SC_2H_5)_3 + CH_3I \rightarrow CH_3PO(OC_2H_4SC_2H_5)_2 + IC_2H_4SC_2H_5.$$

In addition, it was also prepared by the action of β-hydroxydiethyl sulfide on methylphosphonic dichloride in the presence of dimethylaniline:

$$\begin{aligned} &CH_3POCl_2 + 2HOC_2H_4SC_2H_5 + 2C_6H_5N(CH_3)_2 \rightarrow \\ &\rightarrow CH_3PO(OC_2H_4SC_2H_5)_2 + 2C_6H_5N(CH_3)_2 \cdot HCl. \end{aligned} \qquad \text{(VI)}$$

The constants of di-(β-ethylmercaptoethyl) methylphosphonate, prepared by three different methods, are given in the table.

It is possible to prepare similarly di-(β-ethylmercaptoethyl) methylthiophosphonate, (VI)* by starting with methylthiophosphonic dichloride. The di-(β-ethylmercaptoethyl) methylphosphonate readily adds two molecules of methyl iodide or dimethyl sulfate, forming the methiodide (VII) or the methyl methosulfate (VIII) which are readily soluble in water and insoluble in organic solvents:

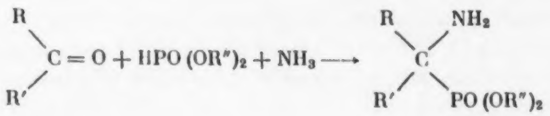
*Eq. is not given in original (Ed.).

$$CH_3PO(OC_2H_4\overset{+}{\underset{J^-}{S}}(CH_3)C_2H_5)_2\ ; \qquad CH_3PO(OC_2H_4\overset{+}{\underset{^-OSO_2OCH_3}{S}}(CH_3)C_2H_5)_2 \qquad \text{(VII) (VIII)}$$

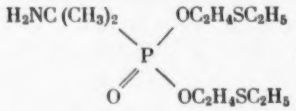
Like the simpler dialkyl hydrogen phosphites, di-(β-ethylmercaptoethyl) hydrogen phosphite reacts with aldehydes [8], for example benzaldehyde:

$$C_6H_5CHO + HPO(OC_2H_4SC_2H_5)_2 \xrightarrow{CH_3ONa} C_6H_5\underset{OH}{C}PO(OC_2H_4SC_2H_5). \qquad \text{(IX)}$$

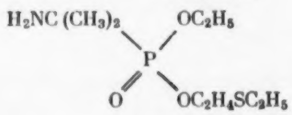
Phosphites (II) and (III) readily react with ketones and ammonia, in the reaction previously discovered by us [9] for dialkyl hydrogen phosphites:



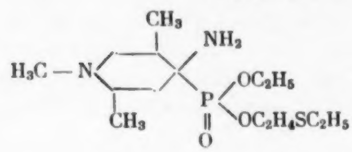
By starting with acetone and 1,2,5-trimethylpiperidone, we prepared di-(β-ethylmercaptoethyl) α-aminoisopropylphosphonate (X), ethyl β-ethylmercaptoethyl α-aminoisopropylphosphonate (XI) and ethyl β-ethylmercaptoethyl 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonate (XII):



; (X)



; (XI)



. (XII)

These substances readily form picrates (XIII) and (XIV).*

EXPERIMENTAL

Tri-(β-ethylmercaptoethyl) phosphite (I). 47.7 g of β-hydroxydiethyl sulfide was added at −5 to 0° to a mixture of 20.7 g (0.15 mole) of phosphorus trichloride, 400 ml of ether and 54.5 g (0.45 mole) of dimethylaniline. The reaction mixture was stirred for one hour at 0° and 30 minutes at room temperature. Then, the dimethylaniline hydrochloride precipitate was filtered off and the ethereal solution was dried over sodium sulfate. The residue after the removal of ether was vacuum distilled. A fraction with b. p. 87-90° ($7 \cdot 10^{-4}$ mm) was isolated; 33 g (64%) colorless sirupy liquid; $n^{20}D$ 1.5213, d^{20}_4 1.1184; found MR 94.42, calculated MR 94.68. The boiling point of the substance at 2 mm was 181-183°, but a partial decomposition takes place under this pressure.

*Equations not given in original. (Ed.).

Found %: C 41.1, 41.4; H 7.8, 7.7; P 8.7, 8.8; S 27.3, 27.6. $C_{12}H_{27}PS_3O_3$. Calculated %: C 41.6; H 7.9; P 8.9; S 27.8.

Di-(β-ethylmercaptoethyl) hydrogen phosphite (II). A. A mixture of 12.1 g (0.1 mole) of dimethylaniline and 10.6 g (0.1 mole) of hydroxydiethyl sulfide was added over one hour with stirring at 7-8° to a solution of 6.9 g (0.05 mole) of phosphorus trichloride in 40 ml of benzene. Then the mixture was stirred for 30 minutes longer, after which 5.3 g (0.05 mole) of β-hydroxydiethyl sulfide was added at the same temperature, and the mixture was again stirred for 30 minutes. Then the dimethylaniline hydrochloride precipitate was filtered off and the filtrate was washed with water, 5 N ammonium hydroxide and again with two portions of water. The benzene solution was then dried over sodium sulfate, after which benzene was distilled off and the residue was fractionated under vacuum. 6.3 g (49%) of the substance with b. p. 110-112° ($7 \cdot 10^{-4}$ mm), $n^{20}D$ 1.5048, d^{20}_4 1.1551, was obtained; found MR 66.33, calculated MR 66.19.

Found %: C 37.5, 37.6; H 7.5, 7.4; P 11.9, 11.6; S 24.9, 24.9. $C_8H_{19}PS_2O_3$. Calculated %: C 37.2; H 7.4; P 12.0; S 24.8.

B. A mixture of 10.6 g (0.1 mole) of β-hydroxydiethyl sulfide and 12.1 g (0.1 mole) of dimethylaniline in 30 ml of benzene was added at 8-10° to 6.9 g (0.05 mole) of phosphorus trichloride in 30 ml of benzene with stirring. After 20 minutes following the addition of the entire mixture, 15 ml of water was added dropwise at the same temperature into the flask. The aqueous layer was separated and the benzene solution was washed with 5% aqueous potassium carbonate, followed by water, after which it was dried over sodium sulfate. After the removal of benzene, the residue was vacuum distilled. 6.7 g (52%) of a colorless liquid with b. p. 112.5-113° ($4 \cdot 10^{-4}$ mm), $n^{20}D$ 1.5057, d^{20}_4 1.1573, was obtained.

Ethyl β-ethylmercaptoethyl hydrogen phosphite (III). A mixture of 10.6 g (0.1 mole) of β-hydroxydiethyl sulfide and 12.2 g (0.1 mole) of dimethylaniline in 65 ml of benzene was added at 7-8° to 14.8 g ((0.1 mole) of ethyl dichlorophosphite in 65 ml of benzene. 25 ml of water was added gradually after 20 minutes of stirring. The aqueous layer was separated and the benzene layer was washed with 5% aqueous potassium hydroxide, followed by water, after which it was dried over sodium sulfate. 6.8 g (34%) of a mobile liquid with b. p. 104-105° (2 mm), $n^{20}D$ 1.4688, d^{20}_4 1.1284, was isolated after distillation; found MR 48.91, calculated MR 48.77.

Found %: C 36.3, 36.3; H 7.6, 7.7; P 15.5, 15.2; S 15.8, 15.8. $C_6H_{15}PSO_3$. Calculated %: C 36.4; H 7.6; P 15.6; S 16.2.

0,0-di-(β-ethylmercaptoethyl) sodium thiophosphate (IV). 5.2 g (0.02 mole) of di-(β-ethylmercaptoethyl) hydrogen phosphite was added over 30 minutes to 0.46 g (0.02 mole) of sodium in 20 ml of benzene. Sodium dissolved completely after heating for 1.5 hours at 40-45°. 0.65 g (0.02 mole) of sulfur was added to the cooled solution and this dissolved rapidly with evolution of heat. Then the mixture was heated for one hour at 50°; benzene was removed and the residue crystallized on being cooled with ice. Three g (48.5%) of colorless needles with m. p. 109-110° was obtained after three recrystallizations from a mixture of ethyl ether and petroleum ether.

Found %: C 30.4, 30.4; H 5.8, 5.7. $C_8H_{18}PS_3O_3Na$. Calculated %: C 30.8; H 5.8.

Di-(β-ethylmercaptoethyl) methylphosphonate (V). A. The sodium derivative was prepared from 0.7 g (0.03 mole) of sodium in 25 ml of ether and 7.75 g (0.03 mole) of di-(β-ethylmercaptoethyl) hydrogen phosphite, by heating for three hours. Then, 4.3 g (0.03 mole) of methyl iodide was added at such a rate that the reaction temperature did not rise above 30-32°. The mixture was then refluxed for three hours. Then, the ether was distilled off and the residue was extracted with benzene. The benzene solution was washed with water. After drying with sodium sulfate, the benzene was removed and the residue was distilled under vacuum. 5.4 g (65%) of a colorless liquid with b. p. 108-109° ($3 \cdot 10^{-4}$ mm), $n^{20}D$ 1.5020, d^{20}_4 1.1404, was obtained; found MR 70.52, calculated MR 70.73.

Found %: C 39.5, 39.8; H 8.0, 7.8; P 10.9, 10.9; S 23.6, 23.6. $C_9H_{21}PS_2O_3$. Calculated %: C 39.6; H 7.8; P 11.4; S 23.5.

B. A mixture of 6.9 g (0.02 mole) of tri-(β-ethylmercaptoethyl) phosphite and 2.8 g (0.02 mole) of methyl iodide was slowly heated on a water bath. The reaction mixture became turbid at 30°. At 56° the

temperature of the reaction mixture rapidly rose to 70°. Then the mixture was heated for one hour at 80°; during this it separated into two layers. The transparent upper layer was separated from the tarry layer (1.3 g; not studied). A fraction with b. p. 43-44° (2 mm) was distilled from the upper layer, and the distillation residue was taken up in 15 ml of benzene, washed with 5 N ammonium hydroxide and water. After being dried with sodium sulfate and after the removal of benzene, the substance was vacuum distilled. 3.1 g (57%) of a colorless liquid with b. p. 108° ($4 \cdot 10^{-4}$ mm), $n^{20}D$ 1.5027, d^{20}_4 1.1448, was isolated; found MR 70.29, calculated MR 70.73.

Found %: C 38.9, 38.7; H 7.7, 7.8; P 11.2, 11.1; S 24.4, 24.2. $C_9H_{21}PS_2O_3$. Calculated %: C 39.6; H 7.8; P 11.4; S 23.6.

C. 10.6 g (0.1 mole) of β-hydroxydiethyl sulfide was added at 0° to a mixture of 6.7 g (0.05 mole) of methylphosphonic dichloride, 12.1 g (0.01 mole) of dimethylaniline and 75 ml of ether, after which the mixture was stirred for five hours at room temperature. The precipitate was filtered off on the following day and the filtrate was washed with 1% hydrochloric acid and water. After being dried over sodium sulfate and after the removal of ether, the residue was vacuum distilled. 8 g (59%) of a colorless liquid with b. p. 111° ($1 \cdot 10^{-3}$ mm), $n^{20}D$ 1.5030, d^{20}_4 1.1412, was isolated; found MR 70.57, calculated MR 70.73.

Found %: C 39.5, 39.7, H 7.7; 7.7; P 11.1, 11.0; S 23.1, 22.9. $C_9H_{21}PS_2O_3$. Calculated %: C 39.6; H 7.8; P 11.4; S 23.5.

Di-(β-ethylmercaptoethyl) methylthiophosphonate (VI). 10.6 g (0.1 mole) of β-hydroxydiethyl sulfide was added with stirring to a mixture of 7.45 g (0.05 mole) of methylthiophosphonic dichloride, 10.1 g (0.1 mole) of triethylamino and 50 ml of benzene. Then the mixture was refluxed for five hours. Ten ml of water was added to the reaction mixture on the following day, with stirring. The benzene layer was separated and washed with 5 N ammonium hydroxide and water. After drying over sodium sulfate, the benzene was distilled off and the residue was vacuum distilled. Three g (21%) of a slightly yellow liquid, with b. p. 123-124° ($1 \cdot 10^{-3}$ mm), $n^{20}D$ 1.5362, d^{20}_4 1.1497, was isolated; found MR 78.25, calculated MR 78.11.

Found %: P 10.4, 10.2; S 33.3, 33.4. $C_9H_{21}PS_3O_3$. Calculated %: P 10.7; S 33.3.

Di-(β-ethylmercaptoethyl) methylphosphonate methiodide (VII). This was obtained by keeping at room temperatue a mixture of 1.42 g (0.01 mole) of methyl iodide and 1.36 g (0.005 mole) of di-(β-ethylmercaptoethyl) methylphosphonate. The substance is a sirupy liquid, readily soluble in hot alcohol and water, insoluble in benzene, chloroform and other organic solvents; 2.7 g (96%) of it was isolated.

Found %: C 23.5, 23.4; H 5.0, 5.1. $C_{11}H_{27}PS_2O_3I_2$. Calculated %: C 23.7; H 4.9.

Di-(β-ethylmercaptoethyl) methylphosphonate methyl methosulfate (VIII). A mixture of 1.36 g (0.005 mole) of di-(β-ethylmercaptoethyl) methylphosphonate, 1.26 g (0.01 mole) of dimethyl sulfate and 5 ml of benzene was heated for three hours on a steam bath. Two layers formed. The benzene layer was separated while the lower layer was washed with dry ether. For a complete removal of ether, the product was heated under vacuum to 40-45°. There was isolated 2.4 g (92%) of a sirupy liquid, readily soluble in water and insoluble in organic solvents.

Found %: C 29.2, 29.1; H 6.3, 6.3. $C_{13}H_{35}PSO_{11}$. Calculated %: C 29.8; H 6.3.

Di-(β-ethylmercaptoethyl) hydroxybenzylphosphonate (IX). Two drops of sodium methoxide solution was added with stirring to a mixture of 0.42 g (0.004 mole) of benzaldehyde and 1.04 g (0.004 mole) of di-(β-ethylmercaptoethyl) hydrogen phosphite. The temperature of the mixture rose to 50°. The mixture was heated for five minutes at 80°, after which it was washed with a sodium bisulfite solution, saturated sodium chloride solution and was taken up in ether and dried over sodium sulfate. 0.7 g (50%) of a colorless sirup was isolated after the removal of ether.

Found %: C 49.3, 49.2; H 6.9, 6.9; P 8.6, 8.6. $C_{15}H_{24}PS_2O_4$. Calculated %: C 49.6; H 6.7; P 8.5.

Di-(β-ethylmercaptoethyl) α-aminoisopropylphosphonate (X) and (XIII). Dry ammonia was passed into a mixture of 15.5 g (0.06 mole) of di-(β-ethylmercaptoethyl) hydrogen phosphite and 5.2 g (0.09 mole) of acetone (the mixture warmed up to 52°). Then the reaction mixture was heated for 15 minutes at 50-60° and for one hour at 100°. After being cooled, the mixture was extracted with ether, the ethereal solution was washed

with water and, after drying over sodium sulfate, the ether was distilled off. The residue was heated on a steam bath under vacuum of 2 mm for 30 minutes, whereupon a low boiling liquid distilled off. The residue, 8.8 g (46.5%) was a transparent, slightly yellow liquid with a weak characteristic odor; $n^{20}D$ 1.5056, d^{20}_4 1.1167; found MR 83.86, calculated MR 83.28.

Found %: C 42.4, 42.3; H 8.4, 8.2; P 9.4, 9.6; S 20.8, 20.8. $C_{11}H_{26}NPS_2O_3$. Calculated %: C 41.9; H 8.4; P 9.8; S 20.3.

The substance decomposes on attempted distillation under high vacuum; it forms a picrate with m. p. 99-100° with an excess of ethereal solution of picric acid.

Found %: C 37.2, 37.3; H 5.4, 5.5; N 10.2, 10.1; P 5.6, 5.4; S 12.0, 11.8. $C_{11}H_{26}NPS_2O_3 \cdot HOC_6H_2(NO_2)_3$. Calculated %: C 37.5; H 5.4; N 10.3; P 5.7; S 11.8.

The base was again liberated by decomposition of the picrate with the calculated amount of alkali. A yellowish liquid was obtained after washing with water and drying in benzene solution over sodium sulfate.

Found %: C 41.7, 41.6; H 8.5, 8.4; N 3.9, 4.2; P 9.7; S 20.1, 20.5. $C_{11}H_{26}NPS_2O_3$. Calculated %: C 41.9; H 8.4; N 4.4; P 9.8; S 20.3.

Ethyl β-ethylmercaptoethyl α-aminoisopropylphosphonate (XI) and (XIV). Dry ammonia was passed into the mixture of 9.9 g (0.05 mole) of ethyl β-ethylmercaptoethyl hydrogen phosphite and 4.4 g (0.075 mole) of acetone (temperature rises to 40°). Then the mixture was heated for 15 minutes at 50-60° and for one hour at 100°. The reaction mixture was extracted with ether, and the ethereal solution was washed with water. After removal of ether, following drying over sodium sulfate, the residue was distilled twice under vacuum. 4.3 g (33.8%) of a yellowish liquid with b. p. 131-132° (3 mm), $n^{20}D$ 1.4778, d^{20}_4 1.0886, was isolated; found MR 66.36, calculated MR 66.05.

Found %: C 42.2, 42.3; H 8.6, 8.7; N 5.1, 5.0; P 11.8, 11.8. $C_9H_{22}NPSO_3$. Calculated %: C 42.3; H 8.7; N 5.5; P 12.1.

A picrate was formed by treatment with excess picric acid in ether; it had m. p. 114-115° after recrystallization from alcohol.

Found %: C 36.9, 36.7; H 5.0, 5.2; N 11.8, 11.8; P 6.8, 6.7; S 6.7, 6.6. $C_9H_{22}NPSO_3 \cdot HOC_6H_2(NO_2)_3$. Calculated %: C 37.2; H 5.2; N 11.6; P 6.4; S 6.6.

Ethyl β-ethylmercaptoethyl 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonate (XII). Dry gaseous ammonia was passed into the mixture of 7.1 g (0.05 mole) of 1,2,5-trimethyl-4-piperidone and 9.9 g (0.05 mole) of the dialkyl hydrogen phosphite; the temperature rose to 36°. With continued passage of ammonia, the reaction mixture,was heated for 1.5 hours at 50-60° and for 2 hours at 100°. After cooling, dry ether was added to the reaction mixture until the precipitation was complete. The precipitate was separated and the ethereal filtrate was washed with water and dried over sodium sulfate. The residue, after the removal of ether, was distilled under vacuum. Three g (18%) of a substance with b. p. 128-132° ($1 \cdot 10^{-4}$ mm), $n^{20}D$ 1.5008, d^{20}_4 1.0952, was isolated; found MR 91.04, calculated MR 90.87.

Found %: C 49.8, 49.8; H 9.1, 9.1; N 7.9, 8.1. $C_{14}H_{31}N_2PSO_3$. Calculated %: C 49.7; H 9.2; N 8.3.

Method of synthesis	Bp, °C; p, mm Hg	n_D^{20}	d_4^{20}	Yield in %
Michaelis-Becker reaction	108—109 ($3 \cdot 10^{-4}$)	1,5020	1,1404	65
Synthesis through the dichloride	111 ($1 \cdot 10^{-3}$)	1,5030	1,1412	59
Arbuzov rearrangement	108 ($4 \cdot 10^{-4}$)	1,5027	1,1448	57

SUMMARY

1. Di-(β-ethylmercaptoethyl) hydrogen phosphite, ethyl β-ethylmercaptoethyl hydrogen phosphite and tris-(β-ethylmercaptoethyl) phosphite were prepared and characterized.

2. Di-(β-ethylmercaptoethyl) hydrogen phosphite has the known properties of dialkyl hydrogen phosphites; it forms the sodium derivative which reacts with sulfur and enters the Michaelis-Becker reaction. Di-(β-ethylmercaptoethyl) hydrogen phosphite reacts with ketones and ammonia, forming esters of α-aminoalkylphosphonic acids; it adds to aldehyde forming esters of hydroxyalkylphosphonic acids.

3. In the Arbuzov rearrangement, tri-(β-ethylmercaptoethyl) phosphite reacts with methyl iodide and forms di-(β-ethylmercaptoethyl) methylphosphonate.

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DETERMINATION OF THE STRENGTH OF THE BOND BETWEEN RADICALS AND SULFUR IN UNSYMMETRIC SULFIDES BY THE METHOD OF DESTRUCTIVE BROMINATION

I. L. Knuniants and N. P. Gambarian

We have already reported the cyclization of substituted amides of β-halo acids into azetidinones under the influence of sodium or potassium amides in liquid ammonia [1]. The success of that work made possible the setting-up of the problem of the synthesis of 4-alkthioazetidin-2-ones by this method. Amides of β-alkthiocarboxylic acids, containing a halogen in the α-position relative to the sulfur atom could serve as starting materials for such a synthesis.

The reaction of carbonyl compounds with mercaptans in the presence of anhydrous hydrogen chloride is being used widely for the synthesis of α-chloro sulfides [2-5]. However the application of this reaction to the interaction of substituted acetoacetamides with benzyl or ethyl mercaptans led only to the corresponding thioacetals * (Tables 1-3):

$$CH_3COCH_2CONHR + R'SH \xrightarrow{HCl} CH_3C(SR')_2CH_2CONHR,$$

where $R = C_6H_5, C_6H_{11}$; $R' = C_2H_5, C_7H_7$.

Similarly fruitless was the application of the method of halogenation [6-8] and hydrohalogenation [9] of thiovinyl ethers to the amides of β-alkthiocrotonic acid. Difficultly separable mixtures were formed in halogenation of the latter, while hydrohalogenation in the presence of aluminum chloride gave the corresponding thioacetals (Tables 1-3). Thus, the only method for the synthesis of such structures was the method of halogenation of amides of β-alkthiocarboxylic acids. As it is known, chlorination of thioethers leads to unstable chlorosulfonium salts which decompose even at room temperature into α-chloro sulfides and hydrogen chloride [10-14]:

$$RSCH_2R' \rightarrow \left[\begin{array}{c} Cl \\ | \\ RSCH_2R' \end{array}\right]^+ Cl^- \rightarrow RSCHClR' + HCl.$$

However sulfides which carry a hydrogen atom in β-position relative to the alkthio group form a difficultly separable mixture of further products of chlorination of the originally formed vinyl ethers [15].

Bromination of the sulfides has hardly been studied at all. Only in 1956 was it shown that a very stable bromosulfonium salt is formed in the treatment of dimethyl sulfide with bromide, this salt decomposing in two directions on prolonged boiling in carbon tetrachloride [16]:

$$CH_3SCH_3 + Br_2 \rightarrow \left[\begin{array}{c} Br \\ CH_3SCH_3 \end{array}\right]^+ Br^- \longrightarrow \left\{\begin{array}{l} \rightarrow CH_3SCH_2Br + HBr \\ \rightarrow CH_3Br + [CH_3SBr] \end{array}\right.$$

*The dibenzyl thioacetal of acetoacetanilide (I) is also formed in the treatment of a mixture of acetoacetanilide with benzyl mercaptan or that of β-benzylmercaptocrotonanilide (II) with concentrated hydrochloric acid. 4-Methylcarbostyril is formed upon dissolution of (I) and (II) in concentrated sulfuric acid.

TABLE 1

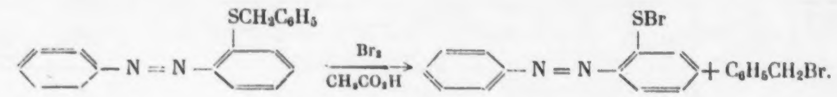
Properties of New, Previously Undescribed Compounds

Ord. No.	Formula of the substance	Found in %				Calculated in %				Recrystallized from	M.p. in °C
		C	H	N	S	C	H	N	S		
1	$C_2H_5SCH_2CH_2CO{-}NHC_6H_{11}$	61,27	9,82		14,34	61,39	9,77		14,9	CCl_4 and petroleum ether	74—75
2	$C_6H_5CH_2SCH_2CH_2{-}CONHC_6H_{11}$	69,20	8,24		11,51	69,31	8,3		11,55	Ethyl acetate	98—99
3	$(CH_3)_3CSCH_2CH_2{-}CONHC_6H_{11}$	64,22	10,47		13,18	64,2	10,8		13,16	Acetone	79—80
4	$(CH_3)_3CSO_2CH_2{-}CH_2CONHC_6H_{11}$	56,78	9,14		11,75	56,73	9,09		11,64	Aqueous alcohol	109—110
5	$C_6H_5CH(SC_2H_5){-}CH_2CONHC_6H_{11}$	70,09	8,72		10,78	70,1	8,59		10,99	Ethyl acetate	107—108
6	$C_6H_5\underset{SC_2H_5}{CH}CH_2CONHC_6H_5$	71,05	6,64			71,58	6,66			»	94—95
7	$C_6H_5\underset{SCH_2C_6H_5}{CH}CH_2CO{-}NHC_6H_{11}$	74,69	7,89			74,9	7,6			Ethyl acetate	92—93
8	$CH_3{-}\overset{SC_2H_5}{C}{=}CHCONH{-}C_6H_{11}$	63,63	9,19			63,44	9,25			»	124—125
9	$CH_3C(SCH_2C_6H_5){=}CHCONHC_6H_5$			5,17				5,12		Alcohol	163,5—164
10	$CH_3{-}\overset{SC(CH_3)_3}{C}{=}CHCONH{-}C_6H_{11}$			5,47				5,49		Ethyl acetate	126—127
11	$CH_3{-}\overset{(SC_2H_5)_2}{C}{-}CH_2CONH{-}C_6H_{11}$	58,72	9,34			58,13	9,34			»	89—90
12	$CH_3{-}\overset{(SC_2H_5)_2}{C}{-}CH_2CONH{-}C_6H_5$	58,74	7,44		22,33	59,36	7,42		22,61	Alcohol	71—72
13	$CH_3C(SCH_2C_6H_5)_2{-}CH_2CONHC_6H_5$	70,33	6,23		15,82	70,76	6,1		15,72	»	97—98
14	$C_2H_5OCH_2CH_2{-}CONHC_6H_{11}$	66,13	10,57	7,12		66,33	10,5	7,04		Ethyl acetate	75—76
15	$CH_3{-}\overset{OCH_3}{C}{=}CCO{-}N(CH_3)C_6H_5$	69,59	7,52	6,89		70,2	7,32	6,78			b. p. 137—138 (4 mm)
16	$CH_3COCH_2CO{-}NHC_6H_{11}$			7,97				7,65		»	74—75

TABLE 1 (continued)

Ord. No.	Formula of the substance	Found in %				Calculated in %				Recrystallized from	M.p. in °C
		C	H	N	S	C	H	N	S		
17	$CH_3-C(=NNHC_6H_3(NO_2)_2)-CH_2CONH-C_6H_{11}$	53,04	5,89				52,89	5,8		Alcohol	206—207
18	$CH_3-C(=NNHC_6H_3(NO_2)_2)-CH_2CO-NHC_6H_5$	53,13	4,24				53,78	4,22		»	197—198
19	$(CH_3)_2C(SH)-CH(CO_2CH_3)-NHCOCH_2-CHBrC_6H_5$		4,09	3,83						Ethyl acetate	121—122
20	$(CH_3)_2C(SH)-CH(CO_2CH_3)-NHCOCH_2-CHBrCH_3$		4,49	4,47						»	105—106
21	$CH_2=CHCONHC_6H_{11}$		8,8	8,89						CCl_4	113—114
22	$ClCH_2CH_2CO-NHC_6H_{11}$		7,39	6,94						CCl_4	109—110
23	$BrCH_2CH_2CO-NHC_6H_{11}$			5,98				6,01		Ethyl acetate	104—105
24	$CH_3CCl=CHCO-NHC_6H_{11}$	59,39	8,04			59,55	7,94			Alcohol	123—123,5
25	$CH_3CCl=CHCO-N(CH_3)C_6H_5$	62,80	5,73			63,07	5,73				b.p.124—125 (3 min)
26	$C_6H_5CH=CBrCO-NHC_6H_{11}$ (trans)			4,55				4,57		CCl_4 and petroleum ether	170—172
27	$C_6H_5CH=CBrCO-NHC_6H_{11}$ (cis)	58,58	5,82			58,44	5,84			Alcohol	89—90
28	$C_6H_5CH=CBrCO-NH_2$			5,93				6,19		CCl_4	104—106
29	$BrCH_2CHBrCO-NHC_6H_5$			5,10				4,56		Alcohol	154—155
30	$BrCH_2CHBrCO-NHC_6H_{11}$			4,78				4,47		»	175—176

The formation of sulfenyl bromide is hypothetical. The author failed to isolate either this substance or its transformation products. In addition, individual examples of cleavage of benzyl sulfides by boiling them with bromine in glacial acetic acid are known [17, 18]:



The initial substituted amides of β-alkthiocrotonic and β-alkthiocinnamic acids were prepared by two routes:

a) $R'CH = CHCONHR'' + RSH \rightarrow R'CH(SR)CH_2CONHR''$;
b) $R'CHXCH_2CONHR'' + RSH \rightarrow R'CH(SR)CH_2CONHR''$,
where $R = C_2H_5,\ C_6H_5CH_2,\ (CH_3)_3C;\ R' = H,\ C_6H_5;\ R'' = C_6H_5,\ C_6H_{11};\ X = Cl,\ Br$.

TABLE 2

$RSCH(R') - CH_2CONHR''$ $\qquad$ $RSC(CH_3) = CHCONHR''$

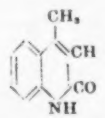
Ord. No.	Starting materials	Reaction product	Reaction conditions	Yield, %
1	$ClCH_2CH_2CONHC_6H_{11}$ and C_2H_5SH	$C_2H_5SCH_2-CH_2CONHC_6H_{11}$	Solution of KNH_2 in liquid ammonia; 1 day	89
2	$CH_2=CHCONHC_6H_{11}$ and C_2H_5SH	$C_2H_5SCH_2-CH_2CO-NHC_6H_{11}$	Liquid ammonia solution 1 day	81
3	Same	Same	KOH in alcohol + ether; about 20°; 1 day	95
4	$ClCH_2CH_2CONHC_6H_{11}$ and $C_6H_5CH_2SH$	$C_6H_5CH_2SCH_2CH_2CO-NHC_6H_{11}$	Same	98
5	$CH_2=CHCONHC_6H_{11}$* and $(CH_3)_3CSH$	$(CH_3)_3CSCH_2CH_2CO-NHC_6H_{11}$	"	92
6	$ClCH_2-CH_2CONHC_6H_{11}$ and $(CH_3)_3CSH$	Same	"	90
7	$C_6H_5CHBrCH_2CONHC_6H_{11}$ and C_2H_5SH	$C_6H_5CH(SC_2H_5)CH_2-CONHC_6H_{11}$	KOH in alcohol + ether; about 20°; 5 days	75
8	$C_6H_5CH=CHCONHC_6H_{11}$* and C_2H_5SH	Same	Same	71
9	$C_6H_5CH=CHCONHC_6H_{11}$* and $C_6H_5CH_2SH$	$C_6H_5CH(SCH_2C_6H_5)-CH_2CONHC_6H_{11}$	KOH in alcohol + ether; about 60°; 10 hours	56
10	$C_6H_5CH=CHCONHC_6H_5$ and C_2H_5SH	$C_6H_5CH(SC_2H_5)-CH_2CONHC_6H_5$	KOH in alcohol + ether; about 20°; 1 day	92
11	$CH_3CCl=CHCONHC_6H_{11}$ and C_2H_5SH	$CH_3-C(SC_2H_5)=CHCONHC_6H_{11}$	KOH in alcohol + ether; about 20°; 2 days	52
12	$CH_3CCl=CHCONHC_6H_5$ and $C_6H_5CH_2SH$	$CH_3-C(SCH_2C_6H_5)=CHCONHC_6H_5$	Liquid ammonia solution; 1 day	57
13	Same	Same	Solution of KNH_2 in liquid ammonia; 1 day	49
14	"	"	KOH in alcohol + ether; about 20°; 2 days	94
15	$CH_3CCl=CHCONHC_6H_{11}$ and $(CH_3)_3CSH$	$CH_3-C(SC(CH_3)_3)=CHCONHC_6H_{11}$	KOH in alcohol + ether; about 60°; 10 hours	54

*Were unable to add tert-butyl mercaptan to cinnamic acid cyclohexylamide.

The reaction was run either in alcohol-ether solution of potassium hydroxide or in solution of potassium amide in liquid ammonia or simply in liquid ammonia solution. The corresponding derivatives of were unable to

TABLE 3

$RC(SR')_2CH_2CONHR''$ and Other Compounds

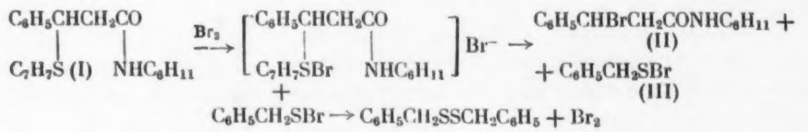
Ord. No.	Starting materials	Reaction product	Reaction conditions	Yield, in %
1	$CH_3COCH_2CONHC_6H_5$ and C_2H_5SH	$CH_3C(SC_2H_5)_2CH_2CO—NHC_6H_5$	Stream of dry HCl, 0°	83
2	$CH_3COCH_2CONHC_6H_{11}$ and C_2H_5SH	$CH_3C(SC_2H_5)_2CH_2CO—NHC_6H_{11}$	Same	77
3	$CH_3COCH_2CONHC_6H_5$ and $C_6H_5CH_2SH$	$CH_3C(SCH_2C_6H_5)_2CH_2—CONHC_6H_5$	Stream of dry HCl in abs. ether sol.	95
4	Same	Same	Conc. HCl; ≈ 20°; 1 day	87
5	$C_6H_5C(SCH_2C_6H_5)=CH—CONHC_6H_5$	$CH_3C(SCH_2C_6H_5)_2CH_2—CONHC_6H_5$	Same	93
6	Same	Same	Stream of dry HCl in absolute ether solution; $AlCl_3$ as catalyst; 2 days	55
7	$CH_3—C(SC(CH_3)_3)=CHCONHC_6H_{11}$	$CH_3—COCH_2CONHC_6H_{11}$	Con. HCl; ≈ 20°; 2 hours	
8	$CH_3C(SCH_2C_6H_5)=CH—CONHC_6H_5$		Conc. H_2SO_4; ≈ 20°; 2 days	
9	$CH_3C(SCH_2C_6H_5)_2CH_2—CONHC_6H_5$	Same	Same	
10	$CH_2=CHCONHC_6H_{11}$ and C_2H_5OH	$C_2H_5OCH_2CH_2CONH—C_6H_{11}$	KOH in alcohol+ether; ≈ 20°; 1 day	73
11	$CH_3CCl=CHCON(CH_3)—C_6H_5$ и CH_3OH	$CH_3—C(OCH_3)=CHCON(CH_3)—C_6H_5$	NaOH in methanol; 70°; 2 hours	72
12	$ClCH_2CH_2COCl$ and $C_6H_{11}NH_2$	$ClCH_2CH_2CONHC_6H_{11}$	Ether sol.; 20°; 0.5 hour	86
13	$CH_2=CHCOCl$ and $C_6H_{11}NH_2$	$CH_2=CHCONHC_6H_{11}$	Same	70
14	$CH_3CCl=CHCOCl$ and $C_6H_{11}NH_2$	$CH_3CCl=CHCONHC_6H_{11}$	NaOH in water; ≈ 20°; 0.5 hour	71
15	$CH_3CCl=CHCOCl$ and $NH(CH_3)C_6H_5$	$CH_3CCl=CHCON(CH_3)—C_6H_5$	Same	78
16	$(CH_3)_2C(HS)—CH(NH_2)—CO_2CH_3$ и $C_6H_5CHBrCH_2COCl$	$(CH_3)_2C(HS)—CH(NHCOCH_2CHBrC_6H_5)—CO_2CH_3$	Ether sol.; 20°; 5 hours	85
17	$(CH_3)_2C(HS)—CH(NH_2)—CO_2CH_3$ и $CH_3CHBrCH_2COCl$	$(CH_3)_2C(HS)—CH(NHCOCH_2CHBrCH_3)—CO_2CH_3$	Same	62
18	$C_6H_5CHBrCHBrCO—NHC_6H_{11}$	$C_6H_5CH=CBrCONHC_6H_{11}$ (trans)	Sol. of KNH_2 in liq ammonia; 1 day	26
19	$C_6H_5CHBrCHBrCO—NHC_6H_{11}$	$C_6H_5CH=CBrCONHC_6H_{11}$ (cis)	KOH in alcohol; ≈ 20°; 10 min	82
20	$C_6H_5CHBrCHBrCO—NH_2$	$C_6H_5CH=CBrCONH_2$	Same	76
21	$BrCH_2CHBrCOCl$ and $NH_2C_6H_5$	$BrCH_2CHBrCONHC_6H_5$	Ether sol.; 20°	89
22	$BrCH_2CHBrCOCl$ and $NH_2C_6H_{11}$	$BrCH_2CHBrCONHC_6H_{11}$	Same	67

β -alkthiocrotonic acid* were formed under the same conditions from amides of β -chlorocrotonic acid. The ease of addition of mercaptans to the amides of α, β -unsaturated carboxylic acids decreases in the following order:

$$C_2H_5SH > C_6H_5CH_2SH > (CH_3)_3CSH \gg C_2H_5OH,$$

while the propionic acid derivatives are formed incomparably more readily than the derivatives of hydrocinnamic acid (Table 1, 2). Halogenation of these amides with sulfuryl chloride or chloro- or bromosuccinimides failed to result in a synthesis of individual substances.**

Bromosulfonium salts precipitated during the bromination of amides of β -alkthiocarboxylic acid (I) by a solution of bromine in carbon tetrachloride, and these lost, even at room temperature, one of the sulfur-bound radicals in the form of bromide (II). The resulting sulfenyl bromide (III) either decomposed forming a disulfide and bromine or added to the initial amide of β -alkthiocarboxylic acid forming the bromide of the corresponding sulfonium base (IV). The latter, in turn, decomposed into the disulfide and bromide (II):



or,

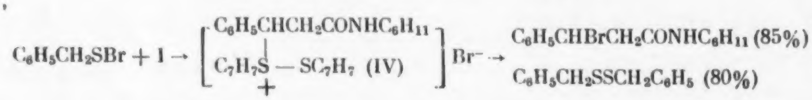


TABLE 4

Ord. No.	Starting material	Reaction product	Yield, % of disulfide	Yield, % of bromide	Remarks
1	$C_6H_5CH(SCH_2C_6H_5)CH_2CONHC_6H_{11}$	$C_6H_5CHBrCH_2CONHC_6H_{11}+$ $+C_6H_5CH_2S-SCH_2C_6H_5$	80	85	
2	$C_6H_5CH(SC_2H_5)CH_2CONHC_6H_{11}$	$C_6H_5CHBrCH_2CONHC_6H_{11}+$ $+(C_2H_5S-SC_2H_5)$		96	
3	$C_6H_5CH(SC_2H_5)CH_2CONHC_6H_5$	$C_6H_5CHBrCH_2CONH(C_6H_5)+$ $+(C_2H_5S-SC_2H_5$		92	
4	$(CH_3)_3CSCH_2CH_2CO-$ $-NHC_6H_{11}$	$SCH_2CH_2CONHC_6H_{11}+$ $\vert$ $SCH_2CH_2CONHC_6H_{11}+$ $+[(CH_3)_3CBr]$	87		
5	$C_6H_5CH_2SCH_2CH_2CO-$ $-NHC_6H_{11}$	$SCH_2CH_2CONHC_6H_{11}$ $\vert$ $SCH_2CH_2CONHC_6H_{11}$ $+C_6H_5CH_2Br$	69,3		Benzaldehyde (24%) is formed simultaneously during hydrolysis

Examples of the cleavage reactions studied by us are collected in Table 4. The destructive bromination reaction proceeds by a single route and in good yields under very mild conditions and may serve, along with von Braun's method [19, 20], for the determination of the bond strength between the radicals and sulfur in unsymmetric sulfides. As it is seen in Table 4, the bond strength of the sulfur with the radicals studied by us increases in order:

*We could not add mercaptans to β -chlorocrotonanilide either under the influence of ultraviolet light, or by the use of mercaptides or peroxides.

**Only in the case of β -ethylmercaptohydrocinnamic cyclohexylamide did we succeed in isolating a low yield of β -chlorohydrocinnamic cyclohexylamide.

$$C_6H_5CHCH_2CONHC_6H_5 \sim C_6H_5CHCH_2CONHC_6H_{11} < C_6H_5CH_2- \sim (CH_3)_3C- <$$
$$< -CH_2CH_2CONHC_6H_{11} \sim C_2H_5.$$

EXPERIMENTAL

General Technique of Preparation of β-Alkthio Derivatives of Saturated and Unsaturated Acids

a) A mixture of the appropriate substituted amide and mercaptan was added to a solution of potassium amide in liquid ammonia or directly to liquid ammonia condensed in a wide-mouth test-tube. Ammonia was evaporated after the completion of the reaction, the residue was treated with water, filtered and recrystallized from appropriate solvent (Tables 1 and 2).

b) A small excess of N solution of potassium hydroxide in absolute ethyl alcohol was added to the solution of the substituted amide and the appropriate mercaptan in ether. The solvents were distilled off after the completion of the reaction and the residue was treated with water, filtered and recrystallized (Tables 1 and 2).

General Technique of Preparation of Thioacetals of Amides of β-Oxo Acids

Dry hydrogen chloride was passed through the solution of the β-oxo acid amide and corresponding mercaptan in absolute ether.* The solvent was removed under vacuum after the completion of the reaction and the residue was recrystallized (Table 3).

Cleavage of β-Substituted Amides of β-Alkthio Carboxylic Acids With Bromine

$(CH_3)_3CSCH_2CH_2CONHC_6H_{11}$ (I). 17.5 ml of 10% bromine solution in carbon tetrachloride was added dropwise, with ice cooling and stirring, to a solution of 2.5 g (0.01 mole) of amide (I) in 30 ml of carbon tetrachloride. An abundant yellow precipitate formed after several minutes. The mixture was kept overnight at room temperature, after which water was added and the whole was stirred. The resulting precipitate was filtered off and recrystallized from dioxane. 1.65 g (87%) of snow-white crystals with m. p. 170-171° was obtained.

Found %: C 58.75; H 8.56; N 7.54; S 16.63. $C_{18}H_{32}N_2O_2S_2$. Calculated %: C 58.09; H 8.6; N 7.53; S 17.2.

The resulting β-mercaptopropionic cyclohexylamide disulfide was suspended in liquid ammonia, after which metallic sodium was added until the decolorization ceased. Ammonia was evaporated at room temperature and the residue was dissolved in water and carefully acidified with ice cooling. The precipitated β-mercaptopropionic cyclohexylamide was filtered off and recrystallized from aqueous dioxane. 0.37 g (74%) of colorless crystals with m. p. 65-67° was isolated.

Found %: C 57.78; H 9.11. $C_9H_{17}NOS$. Calculated %: C 57.75; H 9.09.

β-Mercaptopropionic cyclohexylamide decolorizes alcoholic iodine solution, gives a bright color test with sodium nitroprusside and is readily oxidized to the corresponding disulfide by storage in alkaline solutions.

$C_6H_5CH_2SCH_2CH_2CONHC_6H_{11}$ (II). 3.5 ml of 10% bromine solution in carbon tetrachloride was added dropwise, with ice cooling and stirring, to a suspension of 0.55 g (0.02 mole) of amide (II) in 10 ml of carbon tetrachloride. The bromine was decolorized after several minutes and the complex of (I) with bromine precipitated. The reaction mixture was set aside for one day at room temperature, after which water was added and stirred; a penetrating tear-producing odor of benzyl bromide developed gradually and the oily precipitate solidified. The precipitate was filtered off, washed with water and recrystallized from dioxane. 0.27 g (69.3%) of crystals with m. p. 169-170° which were identical with β-mercaptopropionic cyclohexylamide disulfide were isolated. The filtrate was refluxed for several hours with a dinitrophenylhydrazine solution and the resulting precipitate was filtered off and recrystallized from glacial acetic acid. 0.13 g (24%) of yellow crystals with m. p. 234-235°, identical with benzaldehyde dinitrophenylhydrazone, was isolated.

$C_6H_5CH(SC_2H_5)CH_2CONHC_6H_{11}$ (III). a) 34 ml of 10% bromine solution in carbon tetrachloride was gradually added with stirring and ice cooling to a solution of 5.8 g of (III) in 5 ml of carbon tetrachloride. After a treatment similar to the above, we isolated 5.95 g (96%) of light colored crystals with m. p. 137-138°.

*In case of ethyl mercaptan, an excess of this was used at times instead of the solvent.

Found %: C 58.35; H 6.54; N 4.42. $C_{15}H_{20}NOBr$. Calculated %: C 58.06; H 6.47; N 4.52.

0.5 g of the resulting β-bromohydrocinnamic cyclohexylamide (IV) was dissolved in methyl alcohol and treated with the equimolar amount of a potassium hydroxide solution in methyl alcohol. Some water was added after 20 minutes and the resulting precipitate was filtered off. 0.31 g (84%) of crystals with m. p. 177-178° (from ethyl acetate), identical with cinnamic cyclohexylamide, was isolated. 0.14 g (94%) of crystals with m. p. 108-109°, identical with hydrocinnamic cyclohexylamide was isolated by reduction of 0.2 g of (IV) with sodium in liquid ammonia.

b) A mixture of 0.5 g of (III), 0.7 g of chlorosuccinimide and 0.05 g of diethylamine hydrochloride in 20 ml of carbon tetrachloride was kept for two days at room temperature. Then, the resulting precipitate was filtered off and succinimide, with m. p. 123-124°, which did not give a depression in mixed melting point with authentic succinimide, was leached out with water. The water-insoluble crystals were recrystallized from aqueous alcohol. 0.09 g (19.5%) of crystals with m. p. 121-122°, identical with β-chlorohydrocinnamic cyclohexylamide, was obtained.

$\underline{C_6H_5CH(SCH_2C_6H_5)CH_2CONHC_6H_{11}\ (IV).}$ Eight ml of 10% bromine solution in carbon tetrachloride was gradually added with stirring and ice cooling to a solution of 1.4 g of (IV) in 15 ml of carbon tetrachloride. The resulting precipitate was filtered off on the following day, washed with water and recrystallized from ethyl acetate. 1.05 g (85%) of crystals with m. p. 136-137°, identical with β-bromohydrocinnamic cyclohexylamide, was obtained. 0.4 g (80%) of colorless crystals with m. p. 73-74° (from alcohol), identical with dibenzyl disulfide, was isolated after evaporation of carbon tetrachloride from the filtrate.

$\underline{C_6H_5CH(SC_2H_5)CH_2CONHC_6H_5\ (V).}$ Sixteen ml of 10% bromine solution in carbon tetrachloride was gradually added with stirring and ice cooling to a solution of 2.85 g of (V) in 20 ml of carbon tetrachloride. The resulting precipitate was filtered off on the following day, washed with water and recrystallized from ethyl acetate. 2.8 g (92%) of crystals with m. p. 136-137°, identical with β-bromohydrocinnamic cyclohexylamide, was isolated.

SUMMARY

1. Bromination of β-alkthio derivatives of carboxylic acids leads to the cleavage of C—S bond with formation of a bromo derivative and a disulfide.

2. The reaction of destructive bromination may serve as a means of determination of the strength of the bond of the radicals with sulfur in unsymmetric sulfides. The bond strength of the radicals studied by us increases in the series:

$$C_6H_5\underset{|}{C}HCH_2CONHC_6H_5 \sim C_6H_5\underset{|}{C}HCH_2CONHC_6H_{11} < C_6H_5CH_2- \sim (CH_3)_3C- - < -CH_2CH_2CONHC_6H_{11} \sim C_2H_5.$$

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THE EQUILIBRIUM BETWEEN THE ISO AND THE NORMAL FORMS OF 9-NITROFLUORENE

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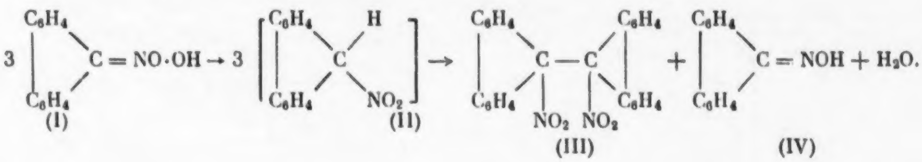
The considerable tendency of the cyclopentadiene ring to capture electron pairs in order to form a stable aromatic sextet [1] appears, specifically, in the unexpected properties of its substituted derivatives. This peculiarity causes the relative stability, color and high dipole moment of fulvenes [2], the stability of cyclopentadienylides [3, 4] and the exceptional properties of diazocyclopentadiene [5]. The ability of cyclopentadiene to strongly attract electrons causes, on the other hand, the instability of cyclopentadienone [6] and its derivatives. As expected, these effects appear in a more or less clearly defined form in two known benzocyclopentadienes – indene and fluorene. Thus, despite the fact that fluorenone is a stable substance, fluorene is able to form its ylides [7] which have bipolar character that is similar to cyclopentadiene ylides, while 9-diazofluorene occupies in this behavior an intermediate position between diazocyclopentadiene and diazophenylmethanes [8].

Nenitzescu and Isacescu [9] showed in one of their previous papers that iso-9-nitrofluorene possesses an unusual stability while the normal form of this nitro compound could not be isolated. The normal form of 9-nitrofluorene that had been described in the literature [10] turned out to be an equimolar mixture of 1,2-dinitro-1,2-dibiphenyleneethane (III) and fluorenone oxime (IV). All attempts to convert the iso-form (I) into the normal form (II) led invariably to the mixture of these two substances. Because of this it was assumed that the normal form of 9-nitrofluorene is an unstable substance which undergoes an irreversible disproportionation:



(I) (II) (III) (IV)

It appeared necessary to reexamine these reactions, mainly for the purpose of establishing the conditions of equilibrium between the iso- and the normal forms and the stability of the latter.

In the present work we started with iso-9-nitrofluorene, synthesized according to Wislicenus and Waldmüller [10] and determined the content of the iso-form in freshly prepared solutions of this substance by Meyer's bromometric method. The results of these determinations are given in Table 1. It was shown by another series of titrations (Table 2) that the solution of iso-9-nitrofluorene in ethanol is sufficiently stable so that the determinations express the true content of the iso-form.

It is evident from the data in Table 1 that the content of the iso-form in freshly prepared solutions changes with the character of the solvent, being highest in a polar solvent – ethanol, and lowest in a nonpolar solvent – benzene, and having intermediate values in solvents of medium polarity such as dioxane, pyridine or mixtures of dioxane with ethanol. These results correspond precisely to those that may be expected if equilibria between the iso- and the normal forms are established in the solutions, since it is known that the more polar solvents favor the formation of the more polar tautomer and vice versa [12].

TABLE 1

Titration of Iso-9-Nitrofluorene in Various Solvents*

Amount			Vol. of 0.2N thiofate sol., in ml		Content of iso-form, %
of 9-nitrofluorene, g	of solvent, ml		calculated	found	
0,2068	Absolute ethanol	60	39,2	35,7	91,1
0,2040	» »	60	38,65	34,5	89,2
0,1834	» »	60	36,7	33,5	91,3
0,2105	Dioxane	25	39,9	24,5	61,4
0,1703	»	25	32,2	19,6	60,8
0,2074	»	60	39,3	30,8	78,4
0,2068	»	60	39,2	31,4	80,1
0,2237	Dioxane Absolute ethanol	25 25	42,4	33,3	78,5
0,2180	» »	25 25	41,3	32,6	78,9
0,2150	Benzene	60	40,8	0,5	1,23
0,2015 Potassium salt	Absolute ethanol	60	32,25	29,3	90,9
0,2460	» »	60	23,30	22,15**	95,0

*The titration was run directly after dissolution.

**Solution of bromine in alcohol, 0.1 N; the titration was run in the presence of ferric chloride.

TABLE 2

Titration of Iso-9-Nitrofluorene in Alcoholic Solution after Various Time Intervals Following the Dissolution

Amount		Time interval in hours after dissolution	Volume of 0.2N thiosulfate sol., ml		Content of iso-form, %
of 9-nitrofluorene, g	of solvent, ml		calculated	found	
0,0270	Ethanol	1	5,12	4,45	87
0,0270	Ethanol	3	5,12	3,50	68,4
0,0270	Ethanol	12	5,12	3,00	58,6
0,0270	Ethanol	24	5,12	—	—*

*The sample fails to give a color test with ferric chloride.

The simplest treatment of these measurements consists of the deduction that in the solution there is indeed established an equilibrium between these two forms but that this equilibrium is being continually shifted in the direction of the normal form since this form decomposes through disproportionation by the scheme shown above. It also follows from data in Table 1 that the equilibrium between the iso- and the normal forms is established at a very great rate. Only in this manner is it possible to explain the extremely small content of the iso-form in the dioxane and, especially, in the benzene solutions. The appropriate measurements were made in the shortest possible periods of time after the preparation of the solutions.

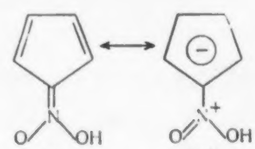
The other conclusion, which follows from the measurements made by us, is that the rate of the disproportionation reaction of the normal form must be smaller than the rate of the reaction of formation of this compound from the iso-form.

$$\text{Iso-form} \xrightarrow[1]{\text{rapid}} \text{normal form} \xrightarrow[2]{\text{slow}} \text{disproportionation products.}$$

Actually, if the rate of reaction 2 were greater than the rate ofReaction 1 (or even if these reactions had a nearly equal rate), the iso form could not exist in solution in measurable, and sometimes large, concentrations (for example in ethanol) since Reaction 1 occurs rapidly as indicated above. In other words, if the rate of Reaction 1 were approximately equal to the rate of Reaction 2, the iso-form would be transformed very soon after its dissolution into its disproportionation products.

If these considerations correspond to reality, one may foresee that in the solvents in which the iso-form eixsts in but small amounts, as for example in benzene, there must exist some appreciable concentrations of the normal, unstable form for a short period after the preparation of the solution, this form being the unknown one. This supposition was checked experimentally and was found to be correct. For this purpose we prepared a benzene solution of iso-9-nitrofluorene in which 1% of iso-form, relative to the amount used originally, was found by titration after one hour following the preparation. The solution was treated with sodium ethoxide, the resulting isonitro derivative was dissolved in water, and the resulting solution was acidified. Iso-9-nitrofluorene was isolated in this manner in amount corresponding to 37% of the amount originally put into solution. It follows that the benzene solution contained the normal form of 9-nitrofluorene in an amount which corresponded to at least 35% of the initially used amount of the iso-form. The benzene solution prepared and treated as indicated above contained after 24 hours only the disproportionation products (III) and (IV).

It follows from these experiments that for 9-nitrofluorene the iso-form is thermodynamically more stable in the crystalline form than is the normal form, in contrast to all other known nitro derivatives of hydrocarbons in which the normal form is stable [12]. An equilibrium is established in solution between the iso- and the normal forms while the latter decomposes at a lower rate than the rate of establishment of the equilibrium but still at sufficiently high rate so that it is impossible to isolate this form. The considerable instability of the iso-form in respect to the normal one is determined by the fact that the electron distribution in the former occurs primarily in accord with the dipolar structure (VI):



(V) (VI)

Attempts to use the bromometric titration for nitrocyclopentadiene were made [13] as they were for 1-nitroindene [14], salts of these substances having been described in the literature. In both cases the solutions of the nitro derivatives in the free state turned out to be too unstable to permit the running of the bromometric determinations.

EXPERIMENTAL

Determination of Content of Iso-Nitro Derivative

The work was done in the following manner by the Meyer method [15]: approximately 10% alcoholic bromine solution was introduced into the freshly prepared and immediately chilled (to −5°) solution of iso-nitro derivative until a permanent yellow color appeared. The colored solution was treated immediately with a 10% alcoholic solution of cyclohexene until it was decolorized, followed by potassium iodide solution. All these operations required not over 30 seconds. The liberated iodine was titrated with standard sodium thiosulfate so ution in the presence of starch. The results of these determinations are given in Table 1.

We also used the method of direct titration of the iso-nitro derivative by an alcoholic solution of 0.1 N bromine in the presence of ferric chloride (the last determination in Table 1). The results of this determination differed but little from those of the indirect method. The results of the determinations are given in Tables 1 and 2.

a) 0.2132 g of iso-9-nitrofluorene was dissolved in 60 ml of absolute benzene. The mixture was treated after one hour, with the solution of sodium ethoxide prepared from 0.05 g of sodium and 5 ml of absolute ethanol. The bright yellow homogeneous solution was extracted with water. The aqueous extract was acidified and the precipitate of iso-9-nitrofluorene was filtered off, washed with water and dried under vacuum over phosphorus pentoxide to constant weight. 0.0800 g of iso-nitrofluorene was isolated in this manner, this amount corresponding to 37% of the originally used amount. The iso-9-nitrofluorene was converted, for identification according to Nenitzescu and Isacescu [9], into 9-iodo-9-nitrofluorene with m. p. 86°.

b) 3.0 g of iso-9-nitrofluorene was dissolved in 900 ml of absolute benzene and the solution was kept at room temperature for 24 hours. The solvent was removed under vacuum at 30-35°. The residue was extracted with 20% potassium hydroxide solution and filtered. The recrystallized precipitate which was dried and washed with benzene had m. p. 175° (1,2-dinitro-1,2-dibiphenyleneethane). The alkaline filtrate yielded on acidification the colorless crystals of fluorenone oxime with m. p. 187°; mixed melting point with authentic fluorenone oxime was 188-190°.

SUMMARY

1. A series of bromometric titrations of solution of iso-9-nitrofluorene in ethanol, dioxane and benzene was run.

2. The iso-form is thermodynamically more stable in the crystalline form than is the normal form; equilibria are established in solution in which the content of the normal form is greater with lower polarity of the solvent. The normal form of 9-nitrofluorene cannot be isolated since it disproportionates forming 1,2-dinitro-1,2-dibiphenylene-ethane and fluorenone oxime. This reaction occurs at a lower rate than the reaction of formation of the normal form from the iso-form. Consequently, temporarily large concentrations of the normal form exist in solution and these were established by a chemical route.

3. The greater stability of the iso-form of 9-nitrofluorene is determined by the tendency of the cyclopentadiene ring to form an aromatic sextet by attracting electron pairs from the nitro group.

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SYNTHESIS OF STEROIDAL COMPOUNDS AND SUBSTANCES RELATED TO THEM

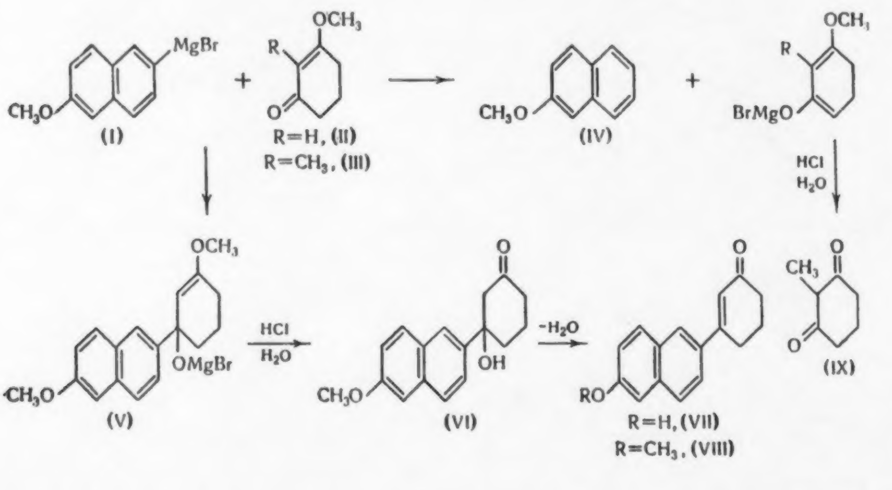
40. SYNTHESIS OF STEROID ANALOGS WHICH DO NOT CONTAIN RING B OR C

I. N. Nazarov and S. I. Zav'ialov

In the previous papers [1-3] we described the synthesis of a series of aromatic compounds which are structurally related to estrone and doisinoleic acid with "cut-out" rings B or C. In continuation of these studies, we prepared in the present work some other model steroid analogs which do not contain rings B or C and which belong to the group of naphthalene and biphenyl derivatives.

The tricyclic methoxy ketone (VIII), obtained previously by another method [4], was formed in a 7% yield by the reaction of 2-bromomagnesium-6-methoxynaphthalene (I) with the enolic ether of dihydroresorcinol (II) and the subsequent hydrolysis of the reaction product (V) with dilute hydrochloric acid. The reaction proceeds through intermediate formation of the keto alcohol (VI) which is readily dehydrated under the conditions of the acid hydrolysis of the enolic ether (V). The low yield of the tricyclic ketone (VIII) is explained by the competing reaction of 2-bromomagnesium-6-methoxynaphthalene with the enolic ether of dihydroresorcinol (II) which is confirmed by the formation of considerable amounts of neroline (IV). This side reaction predominates in the reaction of 2-bromomagnesium-6-methoxynaphthalene with the enolic ether of 2-methyldihydroresorcinol (III) since in this case we were able to isolate only neroline and 2-methyldihydroresorcinol (IX) from the reaction mixture.

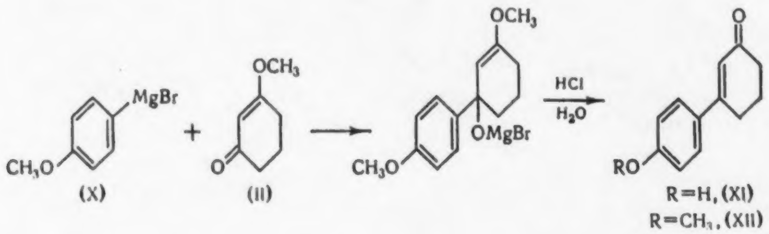
The tricyclic ketone (VIII) on being refluxed briefly in xylene with aluminum chloride undergoes a demethylation with formation of the ketophenol (VII) which is the model analog of homoequilenine.



In contrast to 2-bromomagnesium-6-methoxynaphthalene, p-anisylmagnesium bromide (X) reacts to a considerable degree with the keto form of the enolic ether of dihydroresorcinol, forming after the subsequent hydrolysis with dilute hydrochloric acid a 40% yield of 2-(p-methoxyphenyl)-Δ^1-cyclohexene-6-one, (XII). The

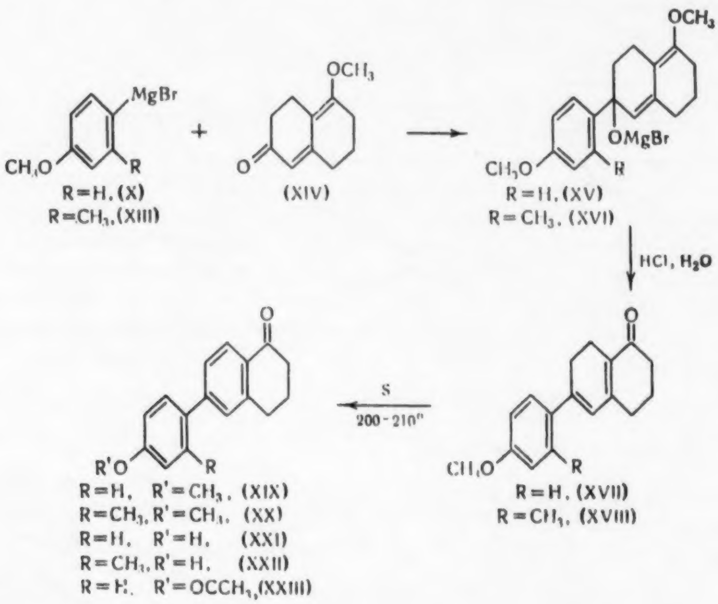
bicyclic ketone (XII), its oxime and the demethylated derivative (XI) turned out to be identical with corresponding compounds formed by another, more complex method [5]. Bicyclic ketone (XII) may be of interest in the synthesis of various model analogs of steroidal hormones.

Bicyclic keto phenol (XI) is close in its structure to the above-described tricyclic analog of homoequilenine (VII).



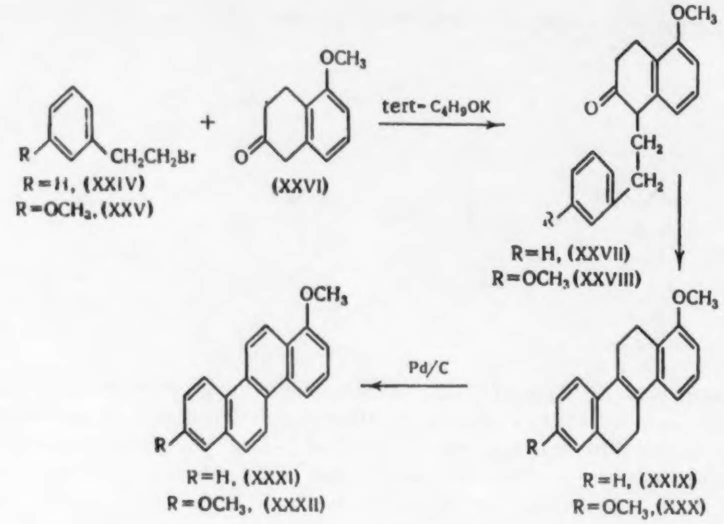
Tricyclic dienic ketones (XVII) and (XVIII), which belong to the group of steroidal analogs with "cut-out" ring B, are formed, as shown earlier [3], in the condensation of p-anisylmagnesium bromide (X) and 4-bromomagnesium-3-methylanisole (XIII) with the enolic ether of $\Delta^{5,10}$-octahydronaphthalene-1,6-dione (XIV) and the subsequent acidic hydrolysis of the reaction products (XV) and (XVI). These dienic ketones are dehydrogenated, on being heated with sulfur, into the biphenyl derivatives (XIX) and (XX).

For physiological tests we also accomplished a demethylation of the methoxy ketones (XIX) and (XX) into the keto phenols (XXI) and (XXII) which correspond to them, by means of aluminum chloride in xylene, and we also ran the acetylation of the tricyclic keto phenol (XXI) into the acetate (XXIII) with acetic anhydride.



5-Methoxytetrahydronaphthyl-2-one (XXVI), the satisfactory method of whose preparation was described in the literature a few years ago [6], may be also used as the starting material for the synthesis of some steroidal compounds and their analogs. We found that the potassium derivative of 5-methoxytetrahydronaphthal-2-one readily yields the corresponding tricyclic ketones (XXVII) and (XXVIII), which may be regarded as steroidal analogs which do not contain ring B, on being heated with 2-phenyl-1-bromoethane (XXIV) and 2-(m-methoxyphenyl)-1-bromoethane (XXV) in tert-butyl alcohol. These tricyclic ketones undergo cyclization and form

chrysene derivatives (XXIX and XXX) on being heated with polyphosphoric acid at 60-70°, while these products are rather smoothly converted into the known 1-methoxychrysene (XXXI) and 1,8-dimethoxychrysene (XXXII) by dehydrogenation with palladium on carbon.*



The homoequilenine analog (VII) possesses according to the literature data [4] estrogenic activity at the 500 γ dose. Ketones (XI), (XVII), (XXI), (XXII) and (XXIII) failed to show any estrogenic activity in tests on castrated mice in doses up to 6 mg.

EXPERIMENTAL**

Reaction of 2-bromomagnesium-6-methoxynaphthalene with enolic ether of dihydroresorcinol. 6.3 g (0.05 mole) of methyl ether of dihydroresorcinol (II), with b. p. 123-124° (19 mm) [9] in 15 ml of ether was added, with ice-water cooling and stirring, to the Grignard reagent prepared from 1.3 g (0.05 g-at) of magnesium and 12 g (0.05 mole) of 2-bromo-6-methoxynaphthalene (m. p. 104-105°) [8] in the mixture of 20 ml of benzene and 15 ml of ether. After standing for 2-3 hours at room temperature, the reaction mixture was decomposed with ice and dilute hydrochloric acid, after which it was heated for one hour at 50-60°. The ether-benzene layer was washed with dilute alkali and after the removal of the solvents the residue was vacuum distilled. 2.4 g of neroline (IV) with m. p. 70-71° and 1.8 g of an oil with b. p. 210-250° (1 mm), from which 0.9 g (7%) of the tricyclic methoxy ketone (VIII) with m. p. 137-138° (from methanol) was isolated, were obtained after the distillation.

Found %: C 80.57, 80.72; H 6.43, 6.44. $C_{17}H_{16}O_2$. Calculated %: C 80.9; H 6.3.

Its oxime melts at 182-183° (from alcohol).

Methoxy ketone (VIII) yields about 50% of the tricyclic keto phenol (VII) with b. p. 211-213° (from alcohol), on being demethylated with aluminum chloride in boiling xylene. Literature [4] gives for methoxy ketone (VIII), its oxime and keto phenol (VII) the following melting points respectively: 138-141°, 171-172° and 215°.

Reaction of 2-bromomagnesium-6-methoxynaphthalene with enolic ether of 2-methyldihydroresorcinol. The reaction was run as described above. From 12 g (0.05 mole) of 2-bromo-6-methoxynaphthalene, 1.3 g (0.05 g-at) of magnesium and 7 g (0.05 mole) of methyl ether of 2-methyldihydroresorcinol (III) with b. p. 98-99° (3 mm) [10], we obtained 3.5 g of neroline (IV), 3.2 g of 2-methyldihydroresorcinol (IX) and 0.5 g of

*These transformations are also described in the paper by Collins and Smith [7], which appeared during the preparation of this paper for press.

**With participation by L. F. Kudriavtseva.

an oil with b. p. 180-230° (1 mm) which could not be crystallized. Similar results were obtained after a longer duration of the reaction.

Reaction of p-anisylmagnesium bromide with enolic ether of dihydroresorcinol. 2.5 g (0.02 mole) of methyl ether of dihydroresorcinol (II) in 15 ml of ether was added with stirring and cooling with ice-water to the Grignard reagent prepared from 7.5 g (0.04 mole) of p-bromoanisole and 1 g (0.04 g-at) of magnesium in 20 ml of ether. After 2-3 hours of standing at room temperature, the mixture was decomposed with ice and dilute hydrochloric acid and was heated for one hour to 50-60°. The ethereal layer was evaporated and the residue was vacuum distilled. 1.6 g of 2-(p-methoxyphenyl)-Δ^1-cyclohexen-6-one (XII) with b. p. 180-185° (2 mm), and m. p. 85-86° (from aqueous alcohol) was isolated.

Its semicarbazone melts at 216-218°. Methoxy ketone (XII) gives a 50% yield of 2-(p-hydroxyphenyl)-Δ^1-cyclohexen-6-one (XI) with m. p. 157-159° (from aqueous alcohol) on being demethylated with aluminum chloride in boiling xylene. Literature [5] gives for the methoxy ketone (XII), its semicarbazone and the demethylated derivative (XI) the following melting points respectively: 84-85°, 218-219° and 159-161.5°.

Dehydrogenation of methoxy ketone (XVIII). A mixture of 2.2 g of methoxy ketone (XVIII) (m. p. 68-69°) [3] and 1 g of sulfur was heated to 200-210° for 15 minutes. The cooled mixture was dissolved in hot methanol and was mixed, after filtration, with a methanolic solution of semicarbazide acetate taken in excess. 1.5 g of the semicarbazone of the tricyclic methoxy ketone (XX) precipitated on standing, this melting with decomposition at 246-247°.

Found %: N 12.58, 12.65. $C_{19}H_{21}O_2N_3$. Calculated %: N 13.0.

The resulting semicarbazone was heated for 30 minutes with 10 ml of 20% hydrochloric acid. 0.8 g (36%) of tricyclic methoxy ketone (XX) with m. p. 88-89° (from heptane) [3] was isolated.

Demethylation of methoxy ketone (XX). 0.8 g of methoxy ketone (XX) and 2 g of aluminum chloride were refluxed with stirring for five minutes in 10 ml of dry xylene. The precipitated phenol was dissolved in hot dilute alkali and was reprecipitated with hydrochloric acid. 0.4 g (53%) of tricyclic keto phenol (XXII) with m. p. 165-167° (from aqueous methanol) was obtained.

Found %: C 80.71, 80.63; H 6.28, 6.35. $C_{17}H_{16}O_2$. Calculated %: C 80.9; H 6.3.

Acetylation of 6-(p-hydroxyphenyl)-1-tetrahydronaphthalone. One g of 6-(p-hydroxyphenyl)-1-tetrahydronaphthalone (XXI) (m. p. 214-215°) [1] was refluxed for 30 minutes with 5 ml of acetic anhydride. After distillation of acetic acid and excess acetic anhydride under vacuum, ether was added to the residue and the resulting precipitate was filtered off. 0.8 g (67%) of 6-(p-acetoxyphenyl)-1-tetrahydronaphthalone (XXIII) with m. p. 138-139° (from a mixture of benzene and iso-octane) was isolated.

Found %: C 76.91, 76. 98; H 5.52, 5.61. $C_8H_{16}O_3$. Calculated %: C 77.2; H 5.7.

Reaction of the potassium derivative of 5-methoxy-2-tetrahydronaphthalone with 2-phenyl-1-bromoethane. Five g of 2-phenyl-1-bromoethane (XXIV) (b. p. 84-86° (8 mm), $n^{20}D$ 1.5570) [11] was added with stirring to the solution of the potassium derivative of 5-methoxy-2-tetrahydronaphthalone prepared from 3.6 g of 5-methoxy-2-tetrahydronaphthalone (XXVI) (b. p. 123-125° (1 mm), $n^{20}D$ 1.5610) [6], 0.8 g of potassium and 15 ml of tert-butyl alcohol. The mixture was heated on a steam bath for one hour in nitrogen atmosphere. The residue after distillation of tert-butyl alcohol under vacuum was treated with water and extracted with chloroform. 2.9 g (51%) of 1-(β-phenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXVII) with b. p. 205-220° (1 mm), $n^{20}D$ 1.5840, was isolated.

Found %: C 81.30, 81.38; H 7.17, 7.18. $C_{19}H_{20}O_2$. Calculated %: C 81.4; H 7.15.

Reaction of the potassium derivative of 5-methoxy-2-tetrahydronaphthalone with 2-(m-methoxyphenyl)-1-bromoethane. The reaction was run as indicated above. From 12 g of 5-methoxy-2-tetrahydronaphthalone, 2.4 g of metallic potassium and 12 g of 2-(m-methoxyphenyl)-1-bromoethane (XXV) with b. p. 130-142° (9 mm) [12] in 100 ml of tert-butyl alcohol, we obtained 9 g (43%) of 1-(m-methoxyphenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXVIII) with b. p. 210-225° (1 mm), and $n^{20}D$ 1.5871.

Found %: C 77.76, 77.71; H 7.28, 7.15. $C_{20}H_{22}O_3$. Calculated %: C 77.4; H 7.1.

Cyclization of 1-(β-phenylethyl)-5-methoxy-2-tetrahydronaphthalone. Four g of 1-(β-phenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXVII) and 40 g of polyphosphoric acid (30 g of phosphoric acid and 10 g of phosphoric anhydride) were heated at 60-70° for five hours. The cooled mixture was treated with a sodium carbonate solution and was extracted with chloroform. 2.6 g of the cyclization product (XXIX) with b. p. 210-220° (1 mm), $n^{20}D$ 1.6492 was isolated.

Found %: C 86.20, 86.11; H 6.79, 6.84. $C_{19}H_{18}O$. Calculated %: C 87.0; H 6.7.

Cyclization of 1-(m-methoxyphenylethyl)-5-methoxy-2-tetrahydronaphthalone. The reaction was run as indicated above. From 3 g of 1-(m-methoxyphenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXVIII) we obtained 0.6 g of the cyclization product (XXX) with m. p. 121-122° (from n-heptane).

Found %: C 81.67, 81.63; H 6.47, 6.54. $C_{20}H_{20}O_2$. Calculated %: C 82.0; H 6.7.

Preparation of 1-methoxychrysene. One g of the above cyclization product of 1-(β-phenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXIX) and 0.5 g of 10% palladium on carbon were heated for 15 minutes to 250-260°. The cooled mixture was extracted with hot chloroform. The crystalline residue, after the removal of the solvent, was washed with methanol. 0.4 g of 1-methoxychrysene (XXXI) with m. p. 176-178° (from a mixture of benzene and petroleum ether) was isolated.

Found %: C 88.11, 88.25; H 5.45, 5.53. $C_{19}H_{14}O$. Calculated %: C 88.4; H 5.4.

Its 2,7-dinitroanthraquinone derivative melts at 284-285° (from xylene).

Literature gives the melting points of 167-168° and 283-284°, respectively, for 1-methoxychrysene and its 2,7-dinitroanthraquinone derivative [13].

Preparation of 1,8-dimethoxychrysene. Two g of the crude cyclization product of 1-(m-methoxyphenylethyl)-5-methoxy-2-tetrahydronaphthalone (XXX) and 0.5 g of 10% palladium on carbon were heated for 20 minutes at 230-240°. The cooled mixture was extracted with chloroform and the solid residue, after the removal of the solvent, was washed with ether. 0.8 g of 1,8-dimethoxychrysene (XXXII) with m. p. 196-198° (from a mixture of benzene and petroleum ether) was isolated.

Found %: C 82.89, 82.96; H 5.69, 5.82. $C_{20}H_{16}O_2$. Calculated %: C 83.3; H 5.6.

Literature [14] cites the m. p. 198-200° for 1,8-dimethoxychrysene.

In conclusion, we express our gratitude to I. A. Eskin for running the tests of the estrogenic activity of the compounds described in this paper.

SUMMARY

1. The unsaturated bicyclic ketone (VIII) was obtained in 7% yield from the reaction of 2-bromomagnesium-6-methoxynaphthalene (I) with the methyl ether of dihydroresorcinol, and on being demethylated gave the model analog of homoequilenine (VII).

2. The reaction of p-anisylmagnesium bromide (X) with the methyl ether of dihydroresorcinol (II) led to the formation of 2-(p-methoxyphenyl)-Δ^1-cyclohexen-6-one (XII) in 40% yield.

3. 6-(p-Hydroxy-o-methylphenyl)-1-tetrahydronaphthalone (XIX) was prepared by demethylation of 6-(p-methoxy-o-methylphenyl)-1-tetrahydronaphthalone (XX) with aluminum chloride in boiling xylene.

4. 6-(p-Hydroxyphenyl)-1-tetrahydronaphthalone (XXI) was converted into 6-(p-acetoxyphenyl)-1-tetrahydronaphthalone (XXIII) by boiling with acetic anhydride.

5. The tricyclic ketones (XXVII) and (XVIII) were isolated respectively by the action of the potassium derivative of 5-methoxy-2-tetrahydronaphthalone (XXVI) on 2-phenyl-1-bromoethane (XXIV) and 2-(m-methoxyphenyl)-1-bromoethane (XXV), and these after the cyclization with polyphosphoric acid and the subsequent dehydrogenation with palladium on carbon gave 1-methoxychrysene (XXXI) and 1,8-dimethoxychrysene (XXXII).

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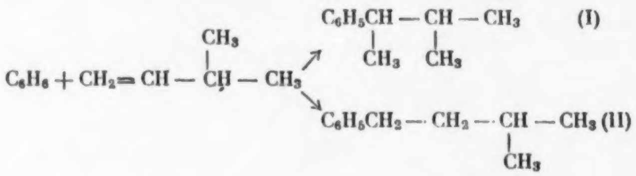
CATALYTIC ALKYLATION OF BENZENE BY ALKENES IN THE VAPOR PHASE

2. ALKYLATION OF BENZENE BY 3-METHYL-1-BUTENE

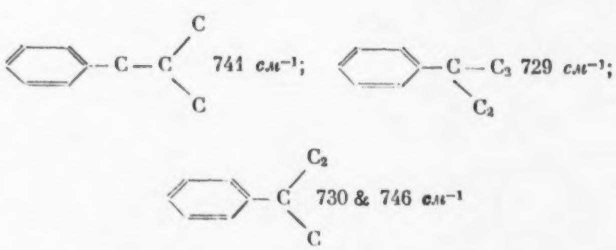
N. I. Shuikin, N. A. Pozdniak and Iu. P. Egorov

The study of the reaction of alkylation of benzene with 3-methyl-1-butene is a continuation of our work in the field of alkylation of benzene in contact with zinc chloride deposited on aluminum oxide [1, 2, 3]. This reaction was studied at pressures from 20 to 50 atmospheres and temperatures from 200° to 350° with various molar ratios of benzene and alkene. The yield of the alkylate in the experiments run by us reached 18.6% calculated on the benzene taken for the reaction and 74.0% calculated on 3-methyl-1-butene. The alkylate consisted of 80% of 2-methyl-2-phenylbutane with b. p. 189-189.5° and 10-15% of a fraction with b. p. above 210°.

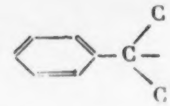
One may expect the formation of two amylbenzenes: 2-methyl-3-phenylbutane (I) and some 2-methyl-4-phenylbutane (II), from the alkylation of benzene by 3-methyl-1-butene:



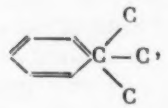
An amylbenzene with b. p. 189-189.5°, $n^{20}D$ 1.4929 and d^{20}_4 0.8736, was isolated from the catalyzate obtained by us. However, this substance was close in its constants to neither (I) nor (II) but to 2-methyl-2-phenylbutane for which the literature [4] gives the following properties: b. p. 189-191°, $n^{20}D$ 1.4920, and d^{20}_4 0.8737. For clarification of this problem we turned to the Raman spectra. It is known [5] that for compounds of type C_6H_5R the Raman spectrum is characterized by the frequencies 621, 1000 and 1031 cm^{-1}. In the presence of simple branches in R, an additional line (or more rarely, two) appears in the region of 720-770 cm^{-1}, for example:

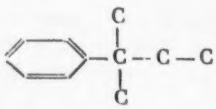


The intensity of these lines is weaker or is of the same order as the intensity of the 621 cm^{-1} lines. In addition, it is known [6] that the quaternary carbon atom in alkanes displays itself by the intense symmetric frequency in the region of 700-750 cm^{-1} which drops to 680-700 cm^{-1} in the presence of a second quaternary or tertiary carbon atom in adjacent position. This appears to be valid also for the aromatic hydrocarbons. Thus, in the

compound  a very bright line at 705 cm^{-1} is observed, this being more intense than the line in the region of 620 cm^{-1} by a factor of four [6].

In the Raman spectrum of the hydrocarbon obtained by us above we observed the following lines (in cm^{-1}): 245 (2 wide), 307 (1 wide), 365 (1), 480 (1 wide), 529 (5), 577 (1), 622 (5), 681 (1), 700 (8), 724 (2), 764 (6), 777 (0), 835 (3 wide) 900 (4), 1000 (10), 1031 (8), 1060 (2), 1085 (3 wide), 1115 (3 wide), 1136 (4), 1195 (3), 1202 (3), 1232 (1), 1302 (2 wide), 1325 (1), 1438 (2 wide), 1460 (6 wide), 1580 (3), 1603 (6), 2870 (5 wide), 2902 (4), 2935 (4), 2968 (5 wide), 3049 (8), 3062 (8).

Taking into account what was said above and comparing the spectrum obtained by us with the spectrum of  of which the intense frequencies (522, 615, 702, 836, 1000, 1030, 1113, 1194 and 1600 cm^{-1}), are close to those of our hydrocarbon (including the characteristic frequency of 702 cm^{-1}) we may assert that the structure of our amylbenzene is that of 2-methyl-2-phenylbutane:



Thus, it may be regarded as proven that the main product of alkylation of benzene with 3-methyl-1-butene under the conditions used by us is 2-methyl-2-phenylbutane. The formation of this hydrocarbon may occur through alkylation of benzene with 2-methyl-1-butene and 2-methyl-2-butene.

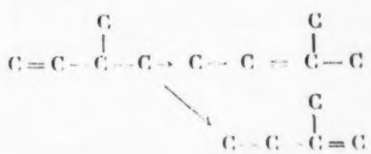
$$C_6H_6 + CH_2 = \overset{\displaystyle CH_3}{\overset{|}{C}} - CH_2 - CH_3 \searrow$$

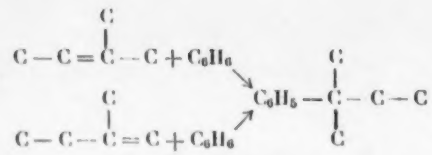
$$\nearrow C_6H_5 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_2CH_3$$

$$C_6H_6 + CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_3$$

Consequently, an isomerization of 3-methyl-1-butene into 2-methyl-1-butene or 2-methyl-2-butene must occur for the formation of 2-methyl-2-phenylbutane. We showed the presence of isopentane, 2-methyl-1-butene and 2-methyl-2-butene, as well as that of an unsaturated hydrocarbon with C_{10} skeleton (evidently amylene dimers), besides 2-methyl-2-phenylbutane, in the catalyzates. Isopentane is probably formed as the result of redistribution of hydrogen in the amylenes.

On the basis of the experimental data obtained, it is possible to suggest the following reaction scheme which operates during the alkylation of benzene with 3-methyl-1-butene in contact with zinc chloride deposited on aluminum oxide:

(I) 

(II) 

EXPERIMENTAL

3-Methyl-1-butene was prepared by dehydration of pure isoamyl alcohol over aluminum oxide at 280° and a thorough fractionation of the catalyzate through a column with 70 theoretical-plate-efficiency. This boiled within 20-22° (755 mm) and had $n^{20}D$ 1.3640 and d^{20}_4 0.6268. These constants were close to those cited for this hydrocarbon in the literature [4]: b. p. 20.06°, $n^{20}D$ 1.3643, d^{20}_4 0.6272. The analysis by the Raman spectrum shows a sufficient purity (98%) of the 3-methyl-1-butene prepared by us.

Catalytic alkylation of benzene with 3-methyl-1-butene was run in an apparatus of the flow type in nitrogen atmosphere, the latter being fed at the rate of 30 ml/min. A mixture of 78 g (1 mole) of benzene and alkene (various amounts, see below) was passed through a space velocity of 0.5 $hour^{-1}$. The catalyzate passed through a spiral trap chilled with dry ice and was collected in a gasometer. From 3.5 to 4.5 liters of gas was collected in each experiment and this gas consisted of 85-90% nitrogen and 8-15% hydrocarbons. The trap contents were added to the main catalyzate which was then subjected to fractionation. Fractions boiling under 81° were distilled through a column with 70 theoretical-plate-efficiency, while fractions boiling over 81° were distilled through one with 20 theoretical-plate-efficiency.

The summary results of the distillation of the catalyzate are given in Tables 1-3. The results of experiments run with various molar ratios of benzene to alkene are given in Table 1 and shown in Fig. 1. The experiments were run at 250° and pressure of 20 atm with space velocity of 0.5 $hour^{-1}$. It is evident from the curves in Fig. 1 that the yield of the alkylate, calculated on the alkene, declines while the yield, calculated on benzene, rises with increasing content of alkene taken for the reaction. The alkylate yield is unchanged by reduction of the space velocity to 0.25 $hour^{-1}$ (Table 1, Expt. No. 5). The amount of pentane-amylene fraction with b. p. 22-40° and that of the intermediate fraction with boiling range of 81-180° in the catalyzate increases with increased content of the alkene in the starting mixture (Table 1). The effect of pressure was followed in experiments at 250° with molar ratios of benzene to alkene of 4:1 and 6:1. It is evident from the results given in Table 2 that the alkylate yield rises with increased pressure. This regularity is also observed in the elevation of the temperature from 200° to 350° (Table 3).

TABLE 1

Alkylation of Benzene with Various Molar Ratios of Benzene to Alkene

No. of expt.	Amount of alkene used, g	Molar ratio of benzene to alkene	Yield of catalyzate, g	Results of distillation of catalyzate, g						
								above 180°		
				22—40°	40—79°	79—81°	81—180°	am'nt. in g	yield, in %, based on benzene	yield, in %, based on alkene
1	5,8	12:1	81,1	1,0	1,0	65,0	1,0	6,1	9,0	73,0
2	11,6	6:1	85,0	3,5	1,3	65,5	2,0	6,4	9,5	38,6
3	17,5	4:1	83,0	1,2	1,3	62,4	3,0	6,7	10,0	27,0
4	35,0	2:1	101,2	10,5	1,2	65,0	6,5	11,3	16,5	22,3
5*	35,0	2:1	101,3	8,0	1,3	63,1	7,0	10,9	16,0	21,6
6	70,0	1:1	143,0	35,0	6,1	68,3	3,5	14,9	22,0	14,9

*Experiment performed with space velocity 0.25 $hours^{-1}$.

TABLE 2

Alkylation of Benzene Under Various Pressures

No. of expt.	Pressure, atm	Molar ratio of benzene to alkene	Catalyzate yield, g	Results of distillation of catalyzate, g						
				22–40°	40–79°	79–81°	81–180°	over 180°		
								Am't. in g	yield, in % of theoretical, on benzene	yield, in % of theoretical, on alkene
1	20	4 : 1	83,5	1,2	1,3	62,4	3,0	10,0	6,7	27,0
2	40	4 : 1	88,3	2,5	1,7	60,5	4,2	16,5	11,3	44,6
3	50	4 : 1	88,0	2,5	1,6	61,3	3,0	18,5	12,5	50,0
4	10	6 : 1	87,3	2,0	1,2	66,0	2,3	8,5	6,0	35,0
5	20	6 : 1	85,5	3,5	1,3	65,5	2,0	9,5	6,4	38,6
6	30	6 : 1	85,1	1,5	1,3	65,0	1,0	14,0	9,5	57,3
7	40	6 : 1	86,0	1,2	1,1	64,5	1,5	15,0	10,1	61,0

TABLE 3

Alkylation of Benzene at Various Temperatures Under 40 Atm Pressure

No. of expt.	Temperature in °C	Molar ratio of benzene to alkene	Catalyzate yield, g	Results of distillation of catalyzate, g						
				22–40°	40–79°	79–81°	81–180°	over 180°		
								am'nt. in g	yield, in % of theoretical, on benzene	yield, in % of theoretical, on alkene
1	200	4 : 1	89,1	6,5	1,0	72,5	2,5	5,0	3,5	13,5
2	250	4 : 1	88,3	2,5	1,7	62,1	4,2	16,5	11,2	44,6
3	300	4 : 1	84,0	2,3	1,3	60,5	4,0	27,5	18,6	74,0
4	300	2 : 1	104,0	9,0	1,4	60,5	3,0	23,0	15,5	31,2
5	350	2 : 1	104,0	15,0	1,5	52,5	2,5	26,1	17,7	35,3
6	350	1 : 1	110,5	25,5	2,0	54,5	2,0	25,5	17,3	17,2
7	350	1 : 2	160,5	37,6	1,8	40,5	3,0	45,0	30,4	18,3

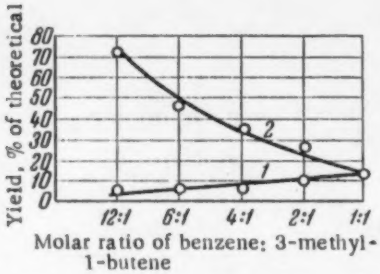
TABLE 4

Results of Distillation of Combined Fractions with B.p. 22-40°

No. of fraction	B.p. in °C	Amount in g	n_D^{20}	d_4^{20}	Unsaturates content, by Margoshes' method, %
I	22–25	9,5	1,3620	0,6270	68,5
II	25–28	25,0	1,3540	0,6268	36,0
III	28–40	25,0	1,3750	0,6540	91,6

The alkylate yield in our experiments reached 74% based on the alkene and 18.6% based on benzene (Table 3, Expt. No. 3). The combined fractions isolated from catalyzates of experiments run at 40 atm and 350° were subjected to an additional study. The amylene fraction with b. p. 22-40° (in amount of 65 g) was distilled through a column with 70 theoretical-plate-efficiency. The results of the distillation are given in Table 4.

The results of the analysis with Raman spectra showed that fractions with b. p. 22-25° at 25-28° consisted of unchanged 3-methyl-1-butene (70 and 30%) and isopentane (30 and 70% respectively). The fraction



Effect of molar ratios of benzene to alkene on the alkylate yield: 1) yield of alkylate in % of theoretical calculated on the benzene used; 2) yield of alkylate in % of theoretical calculated on the alkene used.

with b. p. 28-40° consisted of a mixture of isopentane (10%), 3-methyl-1-butene (20%), 2-methyl-1-butene (30%) and 2-methyl-2-butene (about 40%). The fraction with b. p. 40-79° had $n^{20}D$ 1.4750 and evidently consisted of benzene and amylenes. The fraction with b. p. 79-81° had $n^{20}D$ 1.5000 and consisted of unreacted benzene.

15.1 g of a fraction with b. p. 145-157°, $n^{20}D$ 1.4240, d^{20}_4 0.7550 (iodine number 193) and 10.0 g of a fraction with b. p. 157-162°, $n^{20}D$ 1.4400, d^{20}_4 0.7832 (iodine number 164) were isolated from 45 g of the combined fractions with b. p. 81-180° after repeated fractionation at 756 mm through a column with 20 theoretical-plate-efficiency. Judging by the physicochemical properties, these fractions are close to dimers of pentenes. 60 g (80%) of a hydrocarbon with b. p. 189-189.5°, $n^{20}D$ 1.4929, and d^{20}_4 0.8736, was isolated after fractionation of 75 g of the combined fractions which boiled within 180-210°; found MR* 49.35, calculated MR for $C_{11}H_{16}$ 49.39.

Found %: C 89.02, 89.26; H 10.85, 10.88. $C_6H_5 \cdot C_5H_{11}$. Calculated %: C 89.12; H 10.88.

The Raman spectrum confirmed the proposed structure of the isoamylbenzene obtained by us as that of 2-methyl-2-phenylbutane.

15.0 g of a fraction boiling in the interval of 250-270° was isolated from the combined residues with b. p. above 210°; this had $n^{20}D$ 1.5000 and d^{20}_4 0.8845. It is possible to suppose on the basis of these properties that this consisted mainly of a mixture of diamylbenzenes.

SUMMARY

1. Optimum conditions were found for alkylation of benzene with 3-methyl-1-butene under which the alkylate yield was 18.6% based on benzene used for the reaction and 74% based on the alkene.

2. 2-Methyl-2-phenylbutane is formed instead of the expected 2-methyl-3-phenylbutane and 2-methyl-4-phenylbutane in the alkylation of benzene with 3-methyl-1-butene.

3. 3-Methyl-1-butene isomerizes into 2-methyl-1-butene and 2-methyl-2-butene at 350° and a pressure of 40 atmospheres.

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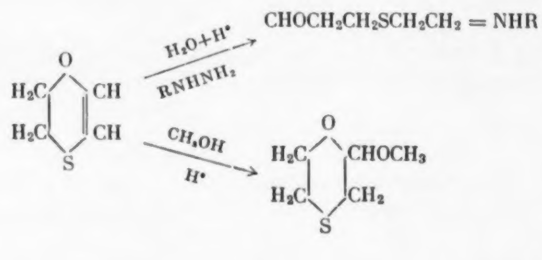
SYNTHESIS OF SULFUR COMPOUNDS BASED ON VINYL ETHERS AND ACETYLENE

17. VINYL ETHERS OF MONOTHIOETHYLENE GLYCOL

M. F. Shostakovskii, E. N. Prilezhaeva and N. I. Uvarova

It was shown in our previous papers [1, 2] that the double bond located in α, β-position relative to a sulfur atom is considerably less active in ionic addition reactions and in polymerizations than the similiar bond which exists under the influence of an oxygen atom. It is also known from the literature [3, 4] that the order of addition of electrophilic reagents, in acid medium, to the double bond of heterocyclic vinyl ethers of the type of p-oxathiene is determined by the orienting influence of the atom of oxygen and not that of sulfur. Actually, the addition of water and of alcohol occurs in accord with the scheme shown below and the isomeric products are not formed at all:



(1)

This difference in the effect on the double bond shown by atoms of oxygen and sulfur depends, in the opinion of the above authors, on the lesser tendency of sulfur to enter into a conjugation with the double bond through its unshared electrons, as compared to that of oxygen:

$$RCH = CH - \ddot{S}R < RCH = CH - \ddot{O}R$$

Some data on the chemical behavior of vinyl ethers of monothioethylene glycol are given in the present paper; the complete vinyl ether of this substance is of interest in that it contains both types of double bonds in the same molecule: O- and S- vinyl ones.

S-Vinyl ether of 1-vinylmercapto-2-hydroxyethane is formed in good yield (70-75%) in the vinylation of monothioethylene glycol, which indicates the relatively greater reactivity, under these conditions, of the mercapto group as compared with the hydroxyl:

$$HOCH_2CH_2SH + CH \equiv CH \xrightarrow[90-105^\circ]{20\%\ KOH} CH_2 = CHSCH_2CH_2OH. \qquad (2)$$

A small amount of bis-(2-hydroxyethylmercapto)ethane is formed as a by-product:

$$CH_2 = CHSCH_2CH_2OH + HSCH_2CH_2OH \rightarrow HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH. \qquad (3)$$

Action of acetylene on the monovinyl ether leads to the formation of the complete ether:

$$CH_2{=}CHSCH_2CH_2OH + CH \equiv CH \xrightarrow[120-135°]{20\%\ KOH} CH_2 = CHSCH_2CH_2OCH = CH_2. \quad (4)$$

The first of these products obtained by us – 1-vinylmercapto-2-hydroxyethane – basically repeats the chemical properties of unsubstituted thiovinyl ethers; some individuality is brought about by the presence of the hydroxy group in its molecule, from which its relatively good solubility follows. Thus, the reaction with mercuric chloride in ethyl alcohol proceeds quantitatively in agreement with the Equation (5) which is usual for thiovinyl ethers [5], while monothioethylene glycol, as shown above in Equation (3), adds readily contrary to the Markovnikov rule:

$$CH_2 = CHSCH_2CH_2OH + HgCl_2 + C_2H_5OH \rightarrow HOCH_2CH_2SHgCl + HCl + CH_3CH(OC_2H_5)_2 \quad (5)$$

However, a mixture of addition products is formed in the reaction with ethyl mercaptan, in contrast with other thiovinyl ethers [6, 1]:

$$HOCH_2CH_2SCH = CH_2 + C_2H_5 \cdot SH \begin{array}{l} \nearrow HOCH_2CH_2SCH_2CH_2SC_2H_5 \\ \searrow CH_3CH\begin{cases} SC_2H_5 \\ SCH_2CH_2OH \end{cases} \end{array} \quad (6)$$

A polymer, evidently having a tridimensional structure from partial cross-linking at the hydroxy groups, is formed under the influence of azoisobutyronitrile; this is insoluble in all the generally used solvents.

TABLE

Comparative Rate of Hydrolysis of Vinyl Ethyl Ether, Vinyl Ethyl Sulfide and Vinyl Ethers of Monothioethylene Glycol (30-35°, 0.001-0.002 mole of vinyl ether, 10 ml of N $NH_2OH \cdot HCl$)

Formula of ether	Duration of hydrolysis, in hours	Amount of acetaldehyde (in moles per mole of ether)	Literature reference
$CH_2 = CHOC_2H_5$	2	0.98; 0.97	[7]
$CH_2 = CHSC_2H_5$	2	0.08; 0.09	[1]
$CH_2 = CHSC_2H_4OH$	3	0.85; 0.855	Present
$CH_2 = CHOCH_2CH_2SCH = CH_2$	3	1.76; 1.86	paper

The effect of the hydroxyl groups is especially strongly reflected in the hydrolysis reaction. 1-Vinylmercapto-2-hydroxyethane is hydrolyzed considerably more rapidly than are other thiovinyl ethers, but somewhat more slowly than in vinyl ethyl ether, in the presence of N hydroxylamine hydrochloride (see Equation (7) and table):

$$HOCH_2CH_2SCH = CH_2 \xrightarrow[NH_2OH,\ HCl]{H_2O,\ H^+} HOCH_2CH_2SH + CH_3CH = NOH + HCl. \quad (7)$$

The complete vinyl ether of monothioethylene glycol reacts with water differently, depending on the hydrolysis conditions and in accord with the different reactivities of its vinyl groups. Thus, at room temperature and in the presence of greatly diluted hydrochloric acid (about 0.02 N) the hydrolysis occurs mainly at the reactive hydroxyvinyl group, while the mercaptovinyl one remains untouched:

$$CH_2=CHSCH_2CH_2OCH=CH_2 \xrightarrow[H_2O]{H^+} HOCH_2CH_2SCH=CH_2+CH_3CHO. \tag{8}$$

Both vinyl groups react with water almost completely under the influence of N hydroxylamine hydrochloride in three hours.

$$CH_2=CHSCH_2CH_2OCH=CH_2 \xrightarrow[NH_2OH\cdot HCl]{H_2O,\ H^+} HOCH_2CH_2SH+CH_3CH=NOH+HCl. \tag{9}$$

Both vinyl groups react with mercuric chloride in aqueous alcohol; the thiovinyl group in accord with the usual scheme, forming the mercurichloride, while the hydroxyvinyl one is hydrolytically cleaved.

$$\begin{array}{l} CH_2=CHSCH_2 \\ \qquad\quad | \\ CH_2=CHOCH_2 \end{array} \xrightarrow{HgCl_2+C_2H_5OH+H_2O} HOCH_2CH_2SHgCl+HCl+CH_3CHO+ \\ +CH_3CH(OC_2H_5)_2. \tag{10}$$

Finally, monothioethylene glycol is readily added to both vinyl groups contrary to the Markovnikov rule:

$$\begin{array}{l} CH_2=CHSCH_2 \\ \qquad\quad | \\ CH_2=CHOCH_2 \end{array} + 2HOCH_2CH_2SH \rightarrow \begin{array}{l} HOCH_2CH_2SCH_2CH_2SCH_2 \\ \qquad\qquad\qquad\qquad | \\ HOCH_2CH_2SCH_2CH_2OCH_2 \end{array} \tag{11}$$

EXPERIMENTAL

Synthesis of 1-Vinylmercapto-2-Hydroxyethane (I)

Twenty-one g (0.27 mole) of monothioethylene glycol, prepared in 40% yield from ethylene chlorohydrin [8], and 3.4 g (0.06 mole) of potassium hydroxide was placed in an autoclave made of stainless steel into which, 10.4 g (0.4 mole) of acetylene was introduced from a cylinder. The reaction mixture was heated with stirring for one hour at 95-100°. The reaction products were dissolved in ethyl ether. The ether insoluble residue was washed down with hot water.

20.0 g of 1-vinylmercapto-2-hydroxyethane (71.4% of theoretical) with b. p. 92-93° (15 mm), $n^{20}D$ 1.5217, was isolated after a vacuum distillation from the ethereal extract, following drying over anhydrous sodium sulfate and removal of ether. The product was soluble in the usual organic solvents and was readily soluble in water.

After repeated distillation: b. p. 70-71° (6 mm), $n^{20}D$ 1.5221, $d^{20}{}_4$ 1.0612; found MR 29.92, calculated MR 29.77.

Found %: C 46.06, 46.34; H 7.73, 7.78; S 30.96, 30.89. C_4H_8OS. Calculated %: C 46.12; H 7.74; S 30.77.

The aqueous extract was evaporated to dryness on a water bath. Colorless plates with m. p. 65° were isolated from the tarry residue (2 g) after many recrystallizations from benzene.

Found %: C 40.00, 40.08; H 7.70, 7.87; S 35.08, 35.24. $C_6H_{14}O_2S_2$. Calculated %: C 39.53; H 7.74; S 35.17.

The substance was bis-(2-hydroxyethylmercapto)ethane, since it gave a negative test with mercuric chloride for the mercaptal group [9].

Reaction of 1-Vinylmercapto-2-Hydroxyethane with Mercuric Chloride

a) To a sample of 1-vinylmercapto-2-hydroxyethane (0.002 mole) in an Erlenmeyer flask, we added 5 ml of 20% mercuric chloride solution in ethyl alcohol. After 24 hours a titration with 0.1 N sodium hydroxide, in the presence of Methyl orange, gave 0.97, 0.96 equivalents of HCl per mole of the ether.

b) 0.25 g of 1-vinylmercapto-2-hydroxyethane was added to 4.5 ml of 20% mercuric chloride solution in ethyl alcohol. The yield of the precipitated mercurichloride of monothioethylene glycol was 0.73 g (97% of theoretical). The substances had the decomposition point of 156-157°, after two recrystallization from ethyl

alcohol. The substance gave no depression in a mixed melting point with the product prepared from monothioethylene ethylene glycol.*

Found %: C 7.88, 7.62; H 1.75, 1.70; Cl 11.28, 11.26. $C_2H_5OSHgCl$. Calculated %: C 7.66; H 1.60; Cl 11.32.

Reaction of 1-Vinylmercapto-2-Hydroxyethane with Ethyl Mercaptan

1.6 g (0.15 mole) of the thiovinyl ether and 1.2 g (0.2 mole) of freshly distilled ethyl mercaptan were mixed in an Erlenmeyer flask. No warm-up of the reaction mixture was observed. After five days, a distillation gave, along with the unreacted mercaptan (0.8 g) and the thiovinyl ether (0.6 g), 0.9 g of a substance with b. p. 140-144° (5 mm), $n^{20}D$ 1.5371. After an additional distillation: b.p. 140-142° (5 mm), $n^{20}D$ 1.5357, d^{20}_4 1.0989; MR found 48.23, MR calculated 47.47.

Found %: C 43.58, 43.62; H 8.55, 8.59. $C_6H_{14}OS_2$. Calculated %: C 43.34; H 8.48.

Titration of the hydrogen chloride liberated by treatment with 20% mercuric chloride solution in ethanol gave the content of mercaptal $CH_3CH\begin{cases} SCH_2CH_2OH \\ SC_2H_5 \end{cases}$ as 13-14%.

Polymerization of 1-Vinylmercapto-2-Hydroxyethane

The polymerization was run in sealed ampul for 28 hours at 60° in the presence of azoisobutyronitrile (0.01 g per 5 g of the substance). The purification of the polymer was complicated, since it dissolved neither in water nor in the usual organic solvents; its ability to swell in ethanol was utilized for the purification. The polymer was heated for four hours with refluxing ethanol until a uniform gel formed and this was poured in a thin stream into cold water, with stirring. The weight of the polymer, after washing with ethyl alcohol and vacuum drying, was 2.0 g (40%).

Found %: C 46.56, 46.70; H 7.89, 7.97; S 29.76, 29.58. $(HOCH_2CH_2SCHCH_2)_n$. Calculated %: C 46.12; H 7.74; S 30.77.

Synthesis of 1-Vinylmercapto-2-Vinyloxyethane (II)

8.6 g (0.082 mole) of 1-vinylmercapto-2-hydroxyethane, 0.9 g (0.016 mole) of potassium hydroxide and 12 g of dioxane were placed in an autoclave, after which acetylene was introduced from a cylinder until it ceased to dissolve at room temperature (4.9 g or 0.18 mole of acetylene). Heating to 120-135° was continued for one hour. The reaction mixture was dissolved in ethyl ether. The extract was filtered from an insoluble tarry precipitate, was dried over anhydrous sodium sulfate and, after the removal of ether and a distillation, yielded 5.0 g of 1-vinylmercapto-2-vinyloxyethane with b. p. 56-58° (8 mm) (yield 50%) and 2.7 g of a tarry residue which was not studied further.

1-Vinylmercapto-2-vinyloxyethane had after a second distillation: b. p. 48-48.5° (7 mm), $n^{20}D$ 1.5000, d^{20}_4 0.9903; found MR 38.71, calculated MR 38.66.

Found %: C55.43, 55.26; H 7.62, 7.68; S 24.78, 24.55. $C_6H_{10}OS$. Calculated %: C 55.34; H 7.74; S 24.62.

Hydrolysis of 1-Vinylmercapto-2-Vinyloxyethane with Aqueous Acid

2.94 g of 1-vinylmercapto-2-vinyloxyethane, 50 ml of water and 10 ml of 0.1 N hydrochloric acid were sealed in an ampul and were mechanically shaken for three hours. The ampul contents were cooled with salt-snow and were extracted with cold ethyl ether (three times; 10 ml each). 0.8 g of 1-vinylmercapto-2-hydroxyethane with b. p. 68-70° (8 mm), $n^{20}D$ 1.5220, was obtained from the ether extract by distillation; the product gave bis-1,2-(2-hydroxyethylmercapto)ethane with m. p. 64° on being mixed with monothioethylene glycol, which gave no mixed melting point depression with the same product prepared from authentic 1-vinylmercapto-2-hydroxyethane. Some 74-75% of acetaldehyde, calculated by Equation (8), was found in the aqueous layer by titration by the hydroxylamine method.

*Literature data for $ClHgSCH_2CH_2OH$: m. p. 135-140°, appear to be in error [8].

Reaction of 1-Vinylmercapto-2-Vinyloxyethane with Mercuric Chloride

a) To a sample of 1-vinylmercapto-2-vinyloxyethane (0.001-0.002 mole) in an Erlenmeyer flask, we added an excess of 20% mercuric chloride solution in ethyl alcohol (5 ml). A colorless precipitated formed immediately. Titration after 24 hours gave: 1.001, 1.004 moles of HCl per one mole of the substance.

b) 12.5 ml of 20% mercuric chloride solution in ethyl alcohol was added to 1.0 g of 1-vinylmercapto-2-vinyloxyethane and the whole was set aside overnight. The weight of the precipitate, after washing with alcohol and ether, was 2.5 g (96.1% of theoretical). The substance decomposed at 156-157° after recrystallization from boiling dioxane and gave no depression in mixed melting point with a sample of authentic monothioethylene glycol mercurichloride.

Reaction of 1-Vinylmercapto-2-Vinyloxyethane with Monothioethylene Glycol

0.75 g (0.06 mole) of 1-vinylmercapto-2-vinyloxyethane was mixed in an Erlenmeyer flask with 0.9 g (0.12 mole) of monothioethylene glycol. The temperature rose to 65° and the reaction mixture crystallized. After two recrystallizations from ethyl ether, we isolated a substance with m. p. 48.5-49° which was readily soluble in ethyl alcohol and water but sparingly soluble in benzene. The substance failed to give an acid test after a treatment with mercuric chloride in ethanol, which indicated the absence of mercaptan groups.

Found %: C 41.90, 41.94; H 7.85, 7.84; S 33.30, 33.34. $C_{10}H_{22}O_3S_2$. Calculated %: C 41.99; H 7.74; S 33.58.

SUMMARY

1. Vinyl ethers of monothioethylene glycol were prepared: 1-vinylmercapto-2-hydroxy- and 1-vinylmercapto-2-vinyloxy-ethanes.

2. It was shown that the double bonds in 1-vinylmercapto-2-vinyloxy-ethane, existing under the influence of oxygen and sulfur respectively, differ noticeably in the ease of ionic addition reactions, especially the reaction of hydrolysis in acid medium.

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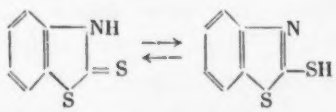
SYNTHESIS OF SULFUR COMPOUNDS BASED ON VINYL ETHERS AND ACETYLENE

18. S-VINYLMERCAPTOBENZOTHIAZOLE

M. F. Shostakovskii, E. N. Prilezhaeva and V. M. Karavaeva

The synthesis of vinyl sulfide of diverse structures is readily accomplished by the reaction of mercaptans with excess acetylene in the presence of alkaline catalysts [1, 2]. It was of interest to prepare some vinyl sulfides which contain nitrogen atoms in the molecule and to study their properties. Mercaptobenzothiazole, "Kaptak," was selected as the starting material for the synthesis of one of such vinyl sulfides, this substance being mainly in the thione form in the crystalline state, as it is known from the literature data [3, 4], but readily passing into the thiol form at high temperatures and in an alkaline medium:


(1)

S-Vinylmercaptobenzothiazole (S-v.m.b.t.) was obtained by the action of acetylene on mercaptobenzothiazole in the presence of potassium hydroxide; the yield of the product was considerably improved when the reaction was run in dioxane medium and when the acetylene concentration was raised (Table 1).

Along with S-vinylmercaptobenzothiazole and a tar, the composition of which was not studied, we isolated potassium mercaptobenzothiazole (K-m.b.t.) from the reaction mixture, with its amount being equivalent to that of the alkali used for the reaction. Later we used potassium mercaptobenzothiazole for the catalyst,since it somewhat improved the yield of the vinylation product. Evidently, the corresponding mercaptide plays the role of the catalyst in vinylation of other substances with thiol groups and the reaction of acetylene with the mercaptide ion (Equation 2) determines the reaction rate.

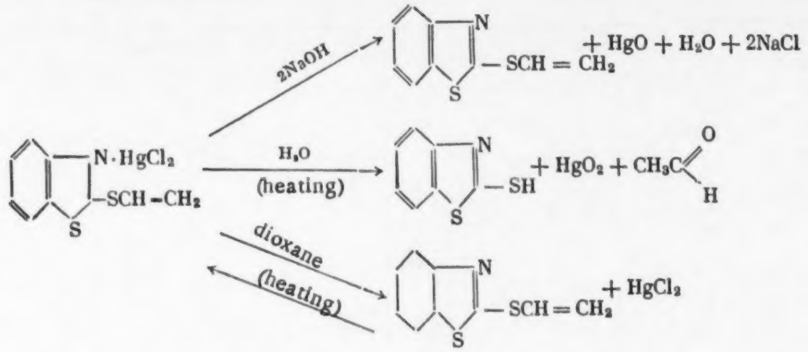
$$CH \equiv CH + SR^- \longrightarrow CH^- = CHSR \qquad (2)$$

$$\overline{CH} = CHSR + RSH \longrightarrow CH_2 = CHSR + SR^- \text{ etc.} \qquad (3)$$

This scheme agrees with the data obtained during the study of the kinetics of vinylation of alcohols [5]. It is easy to explain from this viewpoint why acetylene should preferentially react with the thiol groups, leaving the hydroxy groups of the solvent untouched [6] and leaving the molecule of the reactant similarly untouched [7], the reason for this being the higher nucleophilic nature of the mercaptide ions in comparison with the alkoxy ions [8].

S-Vinylmercaptobenzothiazole is practically colorless in the pure state. However, a product prepared from commercial mercaptobenzothiazole has a bright orange color and darkens rapidly in storage,with the color changing through cherry red to almost black. An attempt to purify this product by the chromatographic route – by passage through a column with silica gel – did not succeed. For the purification we took advantage of the fact that S-vinylmercaptobenzothiazole is not cleaved by mercuric chloride in ethyl alcohol, in contrast to other thiovinyl ethers [1], but yields quantitatively an equimolar complex salt with

with it.* The structure of this salt was confirmed by the following reactions:



(4)

(5)

(6)

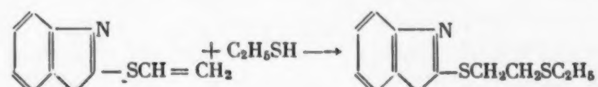
The pure thioether, colorless and not darkening after prolonged storage, was isolated after the decomposition of this complex salt with alkali (Equation 4).

TABLE 1

Synthesis of S-Vinylmercaptobenzothiazole

Used for the reaction		Solvent	React. condit'ns.		Yield of reaction products		
catalyst in mole %	acetylene (moles/mole of mercapto-benzothia-zole		tempera-ture, in °C	time, in hours	S-v.m.b.t. in % of theoreti-cal	K-.m.b.t. in % of theoreti-cal	Tar in % by weight
KOH, 15	1,5	—	170—175	1,5	49,8	13,5	33
KOH, 15	6,1	Dioxane	170—175	2	69,5	13,5	13,3
K-m.b.t.	4,5	»	170—175	1,5	77,8	12,0	10,0

Other reactions of S-vinylmercaptobenzothiazole are similar to those of thiovinyl ethers of the aliphatic series. Thus, ethyl mercaptan adds slowly to it and forms β-ethylmercapto-S-ethylmercaptobenzothiazole:



(7)

A powdery thermofusible polymer is formed in the presence of azoisobutyronitrile, while copolymers containing considerable number of residues with the mercaptobenzothiazole rings are formed with methyl methacrylate and with styrene (Tables 2 and 3). The polymers are slightly hygroscopic, are soluble in benzene and dioxane and are insoluble in petroleum ether, ethyl ether and lower alcohols. Their purification was accomplished by repeated precipitation with methanol from dilute benzene solutions. The melting points were determined in sealed capillaries.

*Such unusual character, for thiovinyl ethers, of the reaction of S-v.m.b.t. with mercuric chloride is evidently explained by the fact that the electrons of the thiovinyl sulfur atom are partially used by conjugation with the thiazole system and the resulting salt has the thione structure:

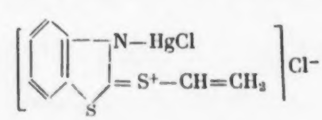


TABLE 2

Polymerization of S-v.m.b.t. and Its Copolymerization with Methyl Methacrylate

Mole fraction in % of S-v.m.b.t. in orig. mixture	Yield of polymeric substances, %	Found in the polymer, in %				Calc. mole frac. in % S-v.m.b.t. in copolymer		M.p. of of polymer in °C (corrected)
		C	H	S	N	on S	on N	
100	30	55,74 55,58	3,62 3,61	33,01 33,21	6,91 6,92	100	100	114—116
75	38	57,27 57,16	4,61 4,77	25,33 25,53	5,66 5,58	63,0	63,3	141—143
50	58	58,12 58,15	5,56 5,54	18,66 18,57	4,14 4,35	39,8	42,3	162—167
25	90	59,64 59,62	6,63 6,62	11,29 21,32	Not determined	21,2	—	198—199

TABLE 3

Copolymerization of S-v.m.b.t. with Styrene (same conditions)

Mole fraction of S-v.m.b.t. in orig. mixture, %	Yield of copolymer %	S found in copolymer, %	Calculated mole frac. of S-v.m.b.t. in copolymer %	M.p. of copolymers in °C (corrected)
75	60,0	25,24	63,1	143—147
50	62,1	17,25	36,8	149—151
25	90,2	11,10	21,3	168—171

EXPERIMENTAL

S-Vinylmercaptobenzothiazole. Commercial mercaptobenzothiazole, which was purified by repeated precipitation with acid from aqueous alkali (m. p. 179°), was used as the starting material. 135 g of mercaptobenzothiazole, 6.5 g of potassium hydroxide and 700 ml of dioxane were placed into a 2.5 – liter rotating autoclave into which acetylene was fed to saturation (135 g of acetylene, or 6.5 moles per mole of mercaptobenzothiazole). This was heated to 170-175° for two hours (maximum pressure – 55 atm). The dioxane solution was filtered by suction from the solid precipitate which was washed with dioxane and dried (weight: 21.4 g; theoretical weight based on KOH used: 23.4 g). M. p. after recrystallization from boiling dioxane was 318-320° (with decomposition). Found: equivalent weight 205.7, 205.2, by titration with N HCl: calculated equivalent weight for $C_7H_4NS_2K$,205.28.

109 g (69.1% of theoretical) of S-vinylmercaptobenzothiazole with b. p. 135-140° (2.5 mm) and 18 g of tar were isolated after the removal of dioxane from the liquid reaction products. The product was bright orange in color. It acquired a light lemon-yellow color after repeated distillations; b. p. 135-136° (2 mm), b. p. 139-141° (3 mm), d^{20}_4 1.2629. The product had a high index of refraction and a high anomalous dispersion: $n^{20}F$ 1.71532; $n^{20}D$ 1.68663; $n^{20}C$ 1.68464; $n^{20}F - n^{20}C$ = 0.03068; found MR 58.36, calculated MR 57.88.*

Found %: C 55.47, 55.93; H 3.75, 3.63; S 33.27, 33.14; N 7.45, 7.35. $C_9H_7NS_2$. Calculated %: C 55.92; H 3.66; S 33.18; N 7.26.

Literature data [6]: b. p. 135-140° (3-2 mm).

S-Vinylmercaptobenzothiazole and mercuric chloride. 7.2 g (equimolar amount) of mercuric chloride

*For calculation of MR, we used the value of atomic refraction of sulfur in aliphatic sulfides: 7.97 [9].

in the form of 20% solution in alcohol was added to 5.1 g of crude S-vinylmercaptobenzothiazole. The immediately formed cheesy precipitate was filtered off, washed with cold alcohol and vacuum dried (11.25 g or 91.8% of theoretical). M. p. 193.2-193.8° (with decomposition) after recrystallization from boiling ether.

Found %: Cl 14.95, 15.16. $C_9H_7NS_2 \cdot HgCl_2$. Calculated %: Cl 15.23.

Titration with 0.1 N sodium hydroxide in the presence of phenolphthalein of a sample of this complex salt gave the equivalent weight of 227.3 and 230.0; calculated equivalent weight of 1/2 $C_9H_7S_2NHgCl_2$: 232.9.

a) 7.2 g of the salt was dissolved in 500 ml of ethyl ether and was decomposed with 5% aqueous potassium hydroxide solution by shaking in a separatory funnel. 2.2 g (73.5% of theoretical) of colorless S-vinylmercaptobenzothiazole with b. p. 127° (1 mm), d^{20}_4 1.2632, was isolated after filtration from the precipitated yellow HgO and after removal of ether. b) 2.0 g of the salt was refluxed in a solution of 20 ml of dry dioxane. Large crystals of mercuric chloride (1.1 g, 91.7%; m. p. 273-275°) precipitated after cooling and removal of part of the dioxane. c) Crystals of mercaptobenzothiazole (0.2 g, 60% of theoretical) precipitated after boiling 0.5 g of the salt with water; the aqueous layer acquired a positive aldehyde reaction (fuchsine-sulfurous acid).

β-Ethylmercapto-S-ethylmercaptobenzothiazole. 19.3 g of vinylmercaptobenzothiazole (0.1 mole), 3.1 g of ethyl mercaptan (0.05 mole) and 0.02 g of azoisobutyronitrile were placed into an ampul blown out with dry nitrogen. No warming-up of the reaction mixture was observed. The ampul was heated for 70 hours at 60°. 0.6 g of unreacted ethyl mercaptan was isolated after the distillation of the reaction products, along with 10.3 g of S-vinylmercaptobenzothiazole and 8.5 g (82.5% based on reacted ethyl mercaptan) of β-ethylmercapto-S-ethylmercaptobenzothiazole with b. p. 190-193° (3 mm). This has b. p. 190-192° (4 mm), b. p. 198° (5 mm) (without decomposition), d^{20}_4 1.2399.

Found %: C 51.87, 51.77; H 5.19, 5.25; S 37.55, 37.59. $C_{11}H_{13}NS_3$. Calculated %: C 51.72; H 5.13; S 37.67.

SUMMARY

S-Vinylmercaptobenzothiazole was prepared and some of its transformations were studied.

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THERMAL POLYMERIZATION OF DIMETHYLBUTENES UNDER HIGH PRESSURES

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In our paper [1] dealing with the polymerization of 2,3-dimethyl-2-butene under pressures up to 27500 atm it was shown that increased pressure leads to a considerable increase of the reaction rate and to a noticeable increase of the average degree of polymerization of that olefin. In this paper we studied in more detail the thermal polymerization of 2,3-dimethyl-2-butene under pressure of about 4000 kg/cm² and temperature of 290°. We also studied the polymerization of two other hexenes: 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene under the same conditions.

EXPERIMENTAL

1. A Study of Kinetics of Polymerization of 2,3-Dimethyl-2-Butene Under Pressure of 3700-4000 kg/cm² and 290°

Pinacolone hydrate was used as the starting material for the synthesis of 2,3-dimethyl-2-butene (and 2,3-dimethyl-1-butene); this, heated with sulfuric acid, yielded pinacoline [2]. The latter was hydrogenated in an autoclave under initial pressure of hydrogen of 140 atm and temperature of 110-150° over Raney nickel. The resulting pinacoline alcohol was passed over zinc chloride deposited on pumice at 200° [3]. The catalyzate was separated from water and was distilled through a fractionating column with 30-theoretical-plate efficiency; 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene were isolated in volume ratio of about 1:3. Each of the isomers was distilled once more through a column from metallic sodium directly before an experiment and the product was sealed, in freshly distilled state, into a lead ampul. The thus obtained isomers were characterized by the following constants: 2,3-dimethyl-2-butene – b. p. 72.8-73.1° (760 mm), d^{20}_4 0.7084, $n^{20}D$ 1.4122. (Literature data [4]: b. p. 73.21° (760 mm), d^{20}_4 0.7080, $n^{20}D$ 1.4122); 2,3-dimethyl-1-butene – b. p. 55.2-55.3° (760 mm), d^{20}_4 0.6775, $n^{20}D$ 1.3900 (Literature data [4]: b. p. 55.64° (760 mm), d^{20}_4 0.6779, $n^{20}D$ 1.3904).

The study of the kinetics of polymerization of 2,3-dimethyl-2-butene was run in lead ampuls with capacity of about 14-15 ml (inner diameter 11 mm, wall thickness 1.5 mm, length of working part 165-170 mm), placed in a steel reactor made of 40 Kh steel. For convenience of loading and unloading, the opening of the reactor was closed by a hydraulic valve closure at one end, this carrying a well for the thermocouple approximately to the middle of the reactor. The ampul, with about 10 g of the substance sealed into it, was placed into the reactor after winding the ampul ends with asbestos to prevent its touching the reactor walls. Then oil was pumped into the reactor up to the pressure of about 1500 kg/cm² at room temperature, the whole was placed into an electric furnace and heating was switched on. When the temperature inside the reactor reached the desired value (290°), the pressure reached 3800-4000 kg/cm². After the passage of the predetermined time interval, the heating was switched off and the furnace was opened; the temperature inside the reactor at this juncture dropped from 290° to 265° over ten minutes. The duration of the experiment was counted from the instant of attainment of the desired temperature in the reactor until the instant of switching-off of the electric heater in the furnace. The experiments differed in the duration (from 2 to 32 hours) and some of the experiments were repeated 2-3 times. The agreement of the results of parallel experiments with duration over five hours was quite satisfactory (see Table 1). The reaction product was unloaded from the ampul after completion of the run and part of the monomer fraction was distilled off with a fractionating column* (diameter: 6.5 mm, length 420 mm) with 30-theoretical-plate efficiency. The residual monomer was distilled from a Claisen flask under vacuum of 150-200 mm, after which the dimer fraction was distilled off on a water bath (under 10 mm vacuum) at 60-78° depending on the duration of the experiment. The liquid residue after the distillation of

*Losses in distillation through the column were 0.1-0.15 g (1-1.5%).

the dimer (polymer with n over 2) was fractionated only in experiment No. 23 (time 32 hours). The bromine numbers of the fractions of polymerizates of 2,3-dimethyl-2-butene, as well as of 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene, were determined according to Kaufmann and Gal'pern [5], while the molecular weights were determined cryoscopically in benzene solution.

The Raman spectra of the dimer fraction of the polymerizates of 2,3-dimethyl-2-butene, 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene were examined in order to be able to judge the composition of these fractions.

The empirical properties, found by Goubeau [6] were used in the study of the dimer fractions, owing to the absence in the literature of any data on the spectra of the majority of olefins $C_{12}H_{24}$; of these properties the first was the line in the region of 1640-1680 cm^{-1}. In the indicated region of each olefin spectrum there was one line whose position, according to Goubeau, depends on the character of substitution of the ethylenic group. The spectral apparatus used by us permitted us to observe three lines in this region in the olefin mixtures: 1640-1645 cm^{-1}, 1650-1660 cm^{-1} and 1665-1680 cm^{-1}. The first of these is due to monosubstituted ethylenes, the second – cis- and unsymmetrically disubstituted ethylenes, and third – trans-disubstituted, tri- and tetra-substituted ethylenes. A further determination of olefin structures by means of the other lines was not always possible.

The results of the kinetic study are given in Table 1.

From the examination of these data it is possible to draw the following conclusions: a) the amount of reacted 2,3-dimethyl-2-butene gradually rises with increased duration of the run and reaches 79.2% at time of 32 hours; at the same time, a corresponding increase of the index of refraction of the reaction products is observed; b) the amount of the resulting dimer fraction at first rises (on the average to 30.7% at time of 16 hours), then slowly begins to decline (to 23.2% at 32 hours) with increased duration of the run. This indicates the stepwise nature of the polymerization process. c) The index of refraction of the dimer fraction and its bromine number decrease with increased duration of the run. At time = 32 hours, the bromine number is 67.4 which corresponds to the content of about 70% unsaturates; d) the index of refraction and the molecular weight of the polymer (with n over 2) rise insignificantly with increased duration of the run.

The results of the vacuum distillation of the entire polymer are given in Table 2 for Experiment No. 23 (time : 32 hours). Fraction I is the dimer fraction and was characterized further (below, along with the dimer fractions from other runs). Fraction II has the average molecular weight which also corresponds to that of the dimer; it is present in relatively small amounts and characterizes the amount of undistilled dimer fraction under the conditions of distillation used by us. The content of unsaturated substances in the polymer fractions with n over 2 was close to 100% and the average molecular weight of the polymer fractions was not great; for example, the molecular weight of the distillation residue (unflowing liquid) corresponded to the degree of polymerization of but 4.3.

We always isolated a small fraction of a substance boiling below the original 2,3-dimethyl-2-butene during the distillation of monomer from the products of polymerization reaction of 2,3-dimethyl-2-butene through the fractionating column. In most of the experiments we selected a first fraction, which amounted to about 1.8 ml. The head fraction contained, from the data secured by examination of the Raman spectra, some 2,3-dimethyl-1-butene, besides the original 2,3-dimethyl-2-butene. Olefins of other types were absent. The head fractions from a number of experiments were combined and distilled through a fractionating column with 30-theoretical-plate efficiency. The characteristics of the first three fractions are given in Table 3.

The distillation curve rises sharply above 58.2° up to the boiling point of 2,3-dimethyl-2-butene. It is possible to conclude, after the examination of the data in Table 3, that the saturated and the unsaturated hydrocarbons, corresponding to the shallow plateau in the distillation curve (56-57°), boil at close temperatures. Actually, about 20% of saturated hydrocarbons are present in fraction I and 50% in fraction III, but the boiling points of these fractions differ only by 1.5-2°. Only 2,3-dimethylbutane (b. p. 57.90° at 760 mm, $n^{20}D$ 1.3750) boils close to 56-57°, among the saturated hydrocarbons. Starting with the supposition that only 2,3-dimethylbutane and 2,3-dimethyl-1-butene are present in fractions I-III (Table 3) and that their indexes of refraction are additive in the mixture, we calculated the content of unsaturates (2,3-dimethyl-1-butene) in the mixture from the index of refraction. The results of the calculation are given in the last column of Table 3 and, as it is evident, these agree satisfactorily with the results obtained on the basis of determination of the bromine numbers.

TABLE 1

Polymerization of 2,3-Dimethyl-2-Butene
(pressure 3700-4000 kg/cm^2, temperature 290°)

No. of expt.	Time in hours	Pressure p in kg/cm^2	$n^{20}D$ of discharged product	Original olefin reacted	Yield of dimer fraction	Polymer yield*	$n^{20}D$ of dimer fraction	Bromine number of dimer fraction***	$n^{20}D$ of polymer*	Bromine number of polymer*	Molecular weight (average) of polymer*
				in % on discharged product**							
14	2	3800—3600	1,4138	4,0							
13	5	3700—3780	1,4159	8,6	5,9	1,6	1,4516		1,4640		
15	5	3780—3810	1,4180	15,0	10,0	4,2	1,4509		1,4617		
18	5	3830—3800	1,4165	11,6	8,0	2,8	1,4513		1,4614		
Average >	5 hours			11,7	8,0	2,9					
10	7	3800—3870	1,4242	30,7	18,4	10,0	1,4500		1,4617		
12	7	3800—3850	1,4222	26,6	17,7	8,0	1,4502	99,5	1,4626		
Average >	7 hours			28,6	18,0	9,0					
6	9	3780—3870	1,4263	34,1	17,8	15,4	1,4492		1,4603		
17	9	3850—3900	1,4250	32,6	20,2	10,8	1,4498		1,4636	78,8	218
Average >	9 hours			33,4	18,5	13,1					
22	12	3820—3990	1,4282	40,5	25,6	13,3	1,4502		1,4644		
19	16	3880—3970	1,4369	58,6	31,1	26,2	1,4493		1,4650		
20	16	3810—3900	1,4359	58,1	30,2	26,8	1,4490	97,0	1,4645		
Average >	16 hours			58,4	30,7	26,5					
21	24	3830—4000	1,4500	77,0	24,7	50,8	1,4478	79,1	1,4670	66,4	240
23	32	3860—4000		79,2	23,2	55,2	1,4470	67,4	1,4683		

*Polymer with n over 2.

**The weight difference between charged and discharged material did not exceed 0.2 g (2%) in all experiments.

***Calculated bromine number for $C_{12}H_{24}$ is 95.2.

TABLE 2

Characteristics of Polymer Fractions from Experiment No. 23 (time 32 hours)

Fraction No.	B.p. in °C (p in mm of mercury)	Content of frac-tion, in %	$n^{20}D$	Molecu-lar weight (average)	Degree of poly-meriza-tion (average)	Bromine number	Content of unsaturates in %
I	60,0— 65,5 (9)	29,3	1,4470				
II	57,0—100 (5)	6,2	1,4526	163	2,0		
III	110 —120 (5)	7,4	1,4597				
IV	120 —147 (5)	24,7	1,4652	241	2,9	62,0	93,0
V	147 —191 (5)	16,3	1,4729	285	3,4	55,5	99,0
Residue		10,5	1,4834	(360) *	(4,3)	44,7	

*The average molecular weight of the residue was calculated from the bromine number assuming that the content of unsaturates in the residue is 100%.

TABLE 3

Characteristics of Fractions I-III, Obtained by Distillation of a Mixture of Head Fractions.

Fraction No.	B.p. in °C (at 760 mm)	Content of the fraction in %	$n^{20}D$	Bromine number	Content of unsaturates calculated from bromine number, in %	Contents of unsaturates calculated from $n^{20}D$ of components of mixture, in %
I	53,7—56,0	6,7	1,3860	144; 152	78,0	71,5
II	56,0—56,5	11,2	1,3852	132; 131	70,0	66,3
III	56,5—58,2	6,7	1,3821	94,9; 94,6	50,0	46,1

TABLE 4

Polymerization of 2,3-Dimethyl-1-Butene at 290°

No. of expt.	Time in hours	Pressure p in kg/cm^2	Amount (in % based on product obtained		
			of unreacted substance	dimer fraction	polymer*
24	2	3780—3700	44,6	11,5	31,2
25	4	3710—3530	75,0	22,0	49,0
26	4	3590—3400	69,3	18,4	47,4
47	4	3850—3690	68,0	17,5	46,0
27	6,5	3750—3160	86,5		
48	4	2040—1950	55,7	18,2	34,0
50	4	3600—3200	66,2	20,5	42,5

*Polymer with n over 2.

TABLE 5

Characteristic of Polymeric Fractions from Experiment No. 25

No. of fraction	B.p. in °C (p in mm of mercury)	Content of fraction, %	$n^{20}D$	Molecular weight (average)	Degree of polymerization (average)	Bromine number	Content of unsaturates in %
I	61,5— 63,0 (9)	7,6	1,4343				
II	50,0— 52,0 (5)	6,2	1,4428				
III	52,0—120 (5)	15,9	1,4504	182	2,2	69,2	78,5
IV	120 —149 (5)	19,9	1,4594	245	2,9	64,9	90,5
Residue		45,5	1,4706	345	4,1	49,5	107

TABLE 6

Properties of Dimer Fractions of 2,3-Dimethyl-1-Butene

No. of fraction	B.p. in °C (p in mm of mercury)	$n^{20}D$	d^{20}_4	Molecular weight	Bromine number	Content of unsaturates in %
I	61,4— 65,4 (11)	1,4325		154	48,0	46,2
II	68,8— 70,5 (10)	1,4417		164	69,5	71,3
I—III	51 —125 (6)	1,4441	0,7906	164	70,5	72,3

TABLE 7

Polymerization of 3,3-Dimethyl-1-Butene at 290°

No. of expt.	Time in hours	Pressure p in kg/cm²	$n^{20}D$ of reaction product	Amount of starting material reacted, in % from prod. obtained
43	1,5	3800—3750	1,4030	33,0
41	3	3770—3625	1,4208	61,0
42	5	3700—3550	1,4279	71,5

The dimer fractions of the polymerizates were separated into two parts (A and B): A — mixture of dimer fractions from experiments with duration up to 16 hours inclusive, with bromine numbers which correspond to the content of about 100% unsaturates; B — mixture of dimer fractions from experiments with duration of 24 and 32 hours, with bromine numbers corresponding to the content of about 70-80% unsaturates. The mixture of dimer fractions A, amounting to 20.5 g,was distilled under vacuum of 9 mm. A fraction with b. p. 68-70° (9 mm), $n^{20}D$ 1.4496, d^{20}_4 0.7968, was isolated; mol. wt. 162; bromine number 102; this fraction comprised 63.7% of the whole mixture. The results of the elemental analysis of this fraction were:

Found %: C 85.83, 85.82; H 14.4, 14.05. $C_{12}H_{24}$. Calculated %: C 85.62; H 14.38.

It was noted above that the yield of the dimer fraction passes through a maximum with increased duration of the polymerization process of 2,3-dimethyl-2-butene. The conclusion about the possibility of a stepwise course of the polymerization was drawn from this fact. In order to determine the ability of the dimer fraction from the polymerizate of 2,3-dimethyl-2-butene to polymerize further, we set up an experiment on polymerization of this dimer fraction under conditions of super-high pressure (at 24700 atm at 290° for five hours).

TABLE 8

Characteristics of Polymeric Fractions of 3,3-Dimethyl-1-Butene *

No. of fraction	B.p. in °C at 20 mm	Content of the fraction in %	$n^{20}D$	d^{20}_4	Mol. weight (aver.)	Degree of polymerization (average)	Bromine number	Content of unsaturates in %
I	69—73	20,9	1,4229	0,7443	153	1,8	79,6	76,0
II	75—140	18,6	1,4316	0,7620	177	2,1		
III	140—200	21,2	1,4472		247	2,9	52,0	80,0
IV	200—232	20,0	1,4578	0,8231	348	4,1	50,0	100
Residue		14,1	1,4688		380	4,5	42,2	100

* A mixture of polymers from all three experiments was distilled (Table 7).

TABLE 9

Polymerization of 2,3-Dimethyl-2-Butene, 2,3-Dimethyl-1-Butene and 3,3-Dimethyl-1-Butene at 290°

Original olefin	No. of expt.	Time in hours	Pressure p in atm	Am'nt. of original olefin reacted, in %, from product obtained	Cont. of prod. w/ aver. degree of polymerization n > 3, in % of total polymer
2,3-Dimethyl-1-butene	23	32	3740—3360	79,4	26,8
2,3-Dimethyl-1-butene	25	4	3410—3590	75,0	45,5
3,3-Dimethyl-1-butene	41,42 & 43	3	3500—3640	61,0*	34,1**

* Conditions and polymer yield are given for experiment No. 41.

** The value was obtained as the result of distillation of a mixture of polymers from all three experiments (Nos. 41-43).

The reaction product was a colorless liquid with average molecular weight of 251 (which corresponds to the average degree of polymerization equal to 3); $n^{20}D$ 1.4677; bromine number 54.4. The content of unsaturates calculated from the molecular weight and the bromine number amounted to 85%. Thus, this experiment showed that the dimer fraction of 2,3-dimethyl-2-butene may undergo a further polymerization. This dimer fraction was examined by taking its Raman spectrum. The results of the study are given in Table 11.

We attempted to discover the reason for the decline of the bromine number of the dimer fraction with increased duration of the polymerization process. For this purpose, the mixture of dimer fractions B was passed through a chromatographic column, having the inner diameter of 9 mm and length of 125 cm, filled with 61 g of silica gel. In all,3.47 g (4.3 ml) was passed through. After this,we obtained the first fraction with b. p. 193° (by Sivolobov method), $n^{20}D$ 1.4447, d^{20}_4 0.8066. The results of analysis follow:

Found %: C 85.99, 86.08; H 14.26, 14.17. $C_{12}H_{24}$. Calculated %: C 85.62; H 14.38.

Examination of this liquid by the method of Raman spectra only permitted affirming that it still contained about 50% of unsaturated hydrocarbons; the remaining 50% were either cyclic or paraffinic hydrocarbons. The results of the elemental analysis speak in favor of the supposition concerning the presence of cyclic hydrocarbons in the dimer fraction. We shall note in this connection that isobutylene dimer cyclizes under pressure at high temperatures (about 400°) into 1,1,3-trimethylcyclopentane [7].

TABLE 10

Properties of Polymeric Fractions of 2,3-Dimethyl-2-Butene, 2,3-Dimethyl-1-Butene and 3,3-Dimethyl-1-Butene

Polymer	B. p. in °C (p in mm of mercury)	Molecular wt.	$n^{20}D$	d^{20}_4	Bromine number	Content of unsaturates in %
Dimer fraction of 2,3-dimethyl-2-butene	68–70 (9)	162	1.4496	0.7968	102	103
Dimer fraction of 2,3-dimethyl-1-butene	51–125 (6)	164	1.4441	0.7906	70.5	72.3
Same	68.8–70.5 (10)	164	1.4417		69.5	71.3
Dimer fraction I of 3,3-dimethyl-1-butene	69–73 (20)	153	1.4229	0.7443	79.6	76.0
Dimer fraction II of 3,3-dimethyl-1-butene	75–140 (20)	177	1.4316	0.7620		
Polymeric fraction of 2,3-dimethyl-2-butene	120–147 (5)	242	1.4652	0.8303	62.0	98.0
Polymeric fraction of 2,3-dimethyl-1-butene	125–159 (6)	234	1.4590	0.8232	60.4	88.5
Polymeric fraction of 3,3-dimethyl-1-butene	200–232 (20)	348	1.4578	0.8231	50.0	109
Polymeric fraction of 2,3-dimethyl-2-butene	147–191 (5)	285	1.4729	0.8476	55.5	99.0
Polymeric fraction of 2,3-dimethyl-1-butene	Residue over 149 (5)	345	1.4706	0.8470	49.5	107
Dimer fraction of 2,3-dimethyl-2-butene (from ionic polymerization) [8]	70–100 (100)		1.4280–1.4351			
Same for 2,3-dimethyl-1-butene [8]	70–111 (100)		1.4257–1.4359			

2. A Study of Polymerization of 2,3-Dimethyl-1-Butene

We ran some experiments on polymerization of 2,3-dimethyl-1-butene in lead ampuls in a reactor with a hydraulic closure at 290°. The results of these experiments are given in Table 4.

In Table 5 are given the results of vacuum distillation of the polymer from Experiment No. 25 (residue after distillation of the monomer). The first three fractions are dimeric. Fractions I and II are characterized in more detail below. The dimer fractions from this experiment amounted to about 30% of the total amount of polymer.

Dimer fractions I (Table 5) were collected from several experiments, owing to the small amount of them, and were distilled under vacuum once more, after which some of the properties of the resulting mixture were determined. The same was done with the fractions II. The properties of these fractions and those of the mixture of fractions I-III from a series of experiments are given in Table 6.

The dimer fractions of the polymerizate of 2,3-dimethyl-1-butene are characterized by the comparatively low content of unsaturates (Tables 5 and 6). The mixture of dimer fractions I-III was examined by means of the Raman spectra. The results of the study are given in Table 11.

TABLE 11

Data on Composition of Dimer Fractions of 2,3-Dimethyl-2-Butene, 2,3-Dimethyl-1-Butene and 3,3-Dimethyl-1-Butene

Structural groups in dimer	Original olefin		
	2,3-dimethyl-2-butene $(CH_3)_2C{=}C(CH_3)_2$	2,3-dimethyl-1-butene $CH_2{=}C(CH_3){-}CH(CH_3){-}CH_3$	3,3-dimethyl-1-butene $CH_2{=}CH{-}C(CH_3)_2{-}CH_3$
$H_2C{=}CH{-}R$	—	+	—
$H_2C{=}C(R){-}R$	—	?	?
$RHC{=}CHR$ (cis)	+ (predominate)	?	+
$RHC{=}CHR$ (trans)	?	?	?
$RHC{=}C(R){-}R$	+	+	?
$R{-}C(R){=}C(R){-}R$	+	+	+

Note: By letter R we designate the alkyl radicals of various structures.

3. A Study of Polymerization of 3,3-Dimethyl-1-Butene

The 3,3-dimethyl-1-butene used by us * was distilled through a column with 30 theoretical-plate efficiency, after which it was characterized by the following constants: b. p. 41.0-41.2° (760 mm), d^{20}_4 0.6530, $n^{20}D$ 1.3760; according to literature data [4]: b. p. 41.24° (760 mm), d^{20}_4 0.6529, $n^{20}D$ 1.3760. The technique of running the experiments was similar to that described above for 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene. The results of the experiments on polymerization of 3,3-dimethyl-1-butene are given in Table 7. By comparing the results of polymerization of 3,3-dimethyl-1-butene with those of polymerization of 2,3-dimethyl-2-butene (Table 1) and 2,3-dimethyl-1-butene (Table 5) it is possible to conclude that 3,3-dimethyl-1-butene polymerizes considerably more rapidly than does 2,3-dimethyl-2-butene and at approximately the same rate as 2,3-dimethyl-1-butene.

The characteristics of the resulting polymer fractions are given in Table 8. The comparative data on polymerization of 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene are given in Table 9. It is possible to conclude, as a result of examination of these data, that not only the rate but also the average degree of polymerization of 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene are noticeably higher than for 2,3-dimethyl-2-butene. Fractions I and II in Table 8 are dimeric; these fractions were examined with the method of Raman spectra. The results of the spectral study of the dimeric fraction are discussed below.

4. On the Composition and the Properties of Polymeric Fractions of 2,3-Dimethyl-2-Butene, 2,3-Dimethyl-1-Butene and 3,3-Dimethyl-1-Butene

Mixtures of dimers, which do not differ in their composition and properties, are formed in ionic polymerization of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene [8], a fact that is connected with the isomerization which occurs under these conditions and which evidently comes to equilibrium. In contrast with this, the polymer fractions, close to each other in molecular weight, which are obtained by thermal polymerization of these hydrocarbons under pressure, differ materially from each other. In Table 10 we give the

* 3,3-Dimethyl-1-butene was kindly provided for us by L. N. Ivanova for which we express our sincere gratitude to her.

characteristics of some polymeric fractions of the isomeric hexenes studies by us, as well as those of dimer fractions obtained in ionic polymerization of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene [8]. It follows from the examination of the data in Table 10 that the indexes of refraction of fractions with close molecular weights decrease in order: 2,3-dimethyl-2-butene, 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene. The specific gravity of the polymer fractions of these hydrocarbons also decrease in the same order. It is further possible to conclude from Table 10 that the dimer fractions obtained in ionic polymerization of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene have considerably lower indexes of refraction than do the dimer fractions of the same olefins obtained by thermal polymerization under pressure.

Data on composition of the dimer fractions of polymerizates of 2,3-dimethyl-2-butene, 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene are given in Table 11, on the basis of the examination of their Raman spectra. The plus sign in Table 11 means the absence of the corresponding structural groups, [this is evidently meant to be "presence" - Ed.] while the minus sign means their absence, or the presence in amounts smaller than 3%, the question mark means possible presence. The data in Table 11 permit us to suppose the existence of a considerable degree of structural isomerization during the thermal polymerization under the conditions used. Actually, if the structural isomerization did not take place, it would have been impossible to expect the formation of cis-dialkylethylenes by dimerization of 2,3-dimethyl-2-butene, while such ethylenes in reality predominate in the mixture. Monoalkylethylenes, whose formation also cannot be visualized with the assumption of a structural isomerization, are present in significant amount in the dimer fraction of 2,3-dimethyl-1-butene. The formation of other olefins, present in the dimer fractions of the hexenes examined by us, may be visualized without this assumption. However, in a number of cases it is necessary to assume the translocation of the double bond. It should be noted that the dimer fractions of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, obtained by ionic polymerization [8], contain about 75% of trialkylethylenes and about 10% of tetraalkylethylenes, i.e., these differ in their composition from the dimer fractions of the same hexenes prepared by the thermal polymerization under pressure.

Examination of the Raman spectra of the head fraction of the monomer fraction distilled from the polymerizate of 2,3-dimethyl-2-butene showed the presence of 2,3-dimethyl-1-butene in it. The content of this olefin, recalculated on the whole monomer fraction, amounts to about 3-4%. No other isomeric hexenes were detected in this head fraction and, hence, their content in this fraction might be less than 3% (accuracy of the method used), i.e., less than 0.2% of the whole monomer fraction. Thus, products of structural isomerization of 2,3-dimethyl-2-butene are absent from the monomer fraction and the presence of an isomer was detected only for a substance that differed from the original hexene in the position of the double bond (2,3-dimethyl-1-butene). Therefore it is more probable that molecules of the dimer or dimer radicals are the units which are subject to structural isomerization in this instance.

It is possible to suppose on the basis of the comparison of the composition and the properties of dimer fractions of polymerizates of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, that the polymerization of 2,3-dimethyl-2-butene does not basically proceed through a stage of a preliminary isomerization of this substance into 2,3-dimethyl-1-butene.

The study of the spectra was done at the Commission on Spectroscopy at the Division for Physico-Mathematical Sciences of the Academy of Sciences USSR by V. T. Aleksanian and Kh. E. Sterin, to whom we express our gratitude.

SUMMARY

1. Thermal polymerization of dimethylbutene under pressures of about 4000 kg/cm^2 was studied.

2. A conclusion about the stepwise character of this reaction was drawn on the basis of investigation of the kinetics of polymerization of 2,3-dimethyl-2-butene under pressure.

3. It was established that thermal polymerization of 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene under pressure proceeds considerably more rapidly than does the polymerization of 2,3-dimethyl-2-butene under similar conditions and leads to formation of polymers with greater average molecular weight.

4. On the basis of comparison of the properties and the composition of the dimer fractions of polymerizates of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, we made the supposition that the polymerization

of 2.3-dimethyl-2-butene does not basically proceed through a step of preliminary isomerization of this substance into 2,3-dimethyl-1-butene. The data on the composition of the dimer fractions also permitted us to conclude that,under the conditions used,a structural isomerization of molecules of the dimers or the radicals $C_{12}H_{23}$ evidently occurs, along with a translocation of the double bond.

5. Thermal polymerization of 2,3-dimethyl-2-butene under high pressure leads to formation of olefins which differ from the products of its ionic polymerization both in composition and in properties, specifically in the higher index of refraction.

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HYDROLYTIC CLEAVAGE OF MESITYL OXIDE AND DEALDOLIZATION OF DIACETONE ALCOHOL OVER TRICALCIUM PHOSPHATE

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The concept of the possibility of formation of unstable, intermediate surface compounds during heterogeneous catalysis has been receiving a wider and wider recognition in recent years. If valid, one may expect a considerable similarity in the mechanisms of homogeneous and heterogeneous catalytic reactions. The reactions of hydrolytic cleavage of mesityl oxide and dealdolization of diacetone alcohol over tricalcium phosphate were studied from this point of view in the present work. It is known that these reactions proceed at a great rate in the liquid phase in the presence of H^+ and OH^- ions. The results obtained by us indicated that the hydrolytic cleavage of mesityl oxide is realized readily over a solid catalyst and , like the reaction in the liquid phase, proceeds through the hydration stage. At the same time, we were the first to show the activity of tricalcium phosphate in the hydration reaction, this substance being already known as a catalyst for reactions of hydrolysis [1] and dehydration [2, 3].

Zangirolami [4] was the first to study the possibility of acceleration of the hydration process by means of solid catalysts. The maximum conversion into acetone (32%) occurred over silica gel in the temperature interval of 200-300° and at molar ratio of water : mesityl oxide about 6. The conversion into acetone amounted to 10% over aluminum oxide under the same conditions, while it was not observed at all over thorium oxide and pumice. McAllister, Bailey, and Bouton [5] showed that acetic acid and isobutylene are obtained during the cleavage of mesityl oxide over a silicophosphate catalyst at 300°. It was supposed that the reaction proceeded by the equation: $(CH_3)_2C = CHCOCH_3 \rightarrow (CH_3)_2C = CH_2 + CH_2 = C = O$ and the acetic acid was formed from ketene. The catalyst was rapidly deactivated in the absence of water. Mesityl oxide was converted almost completely into acetic acid and isobutylene in the presence of water vapor; not more than 10% of acetone was formed.

Kagan and Fal'kovskii [6] observed that up to 65% of mesityl oxide was converted into acetic acid and isobutylene by the passage over an aluminosilicate cracking catalyst at 300° with excess water vapor. It was also shown [7] that the degree of conversion of mesityl oxide, and the acetone yield, increase with increase of the ratio of water : mesityl oxide. At the molar ratio of 14.5, mesityl oxide was converted to the extent of 50% into acetic acid and isobutylene after a single pass, with 39% conversion into acetone. The transformation of mesityl oxide acid rose from 6.8% to 68.7% by the elevation of temperature from 200° to 400°, the yield of acetone decreasing from 56% to 14.9%. Mesityl oxide was unchanged under the same conditions at 300° in the absence of a catalyst.

It is evident, after a review of the literature data, that the reaction proceeds, over the examined solid catalysts, to a considerable extent in a direction that is different from that taken in acidic and alkaline media. The main reaction products in this case are isobutylene and acetic acid, and not acetone.

EXPERIMENTAL

1. The study was run in apparatus of the flow type. Twenty ml of the catalyst was placed in a Pyrex tube. The temperature was measured with a thermocouple, one end of which was placed into the catalyst layer. The reacting components were fed uniformly into the catalyst by means of a piston metering pump with a clockwork mechanism [8]. Water was preliminarily evaporated in a supply tube provided with an electric heater. The

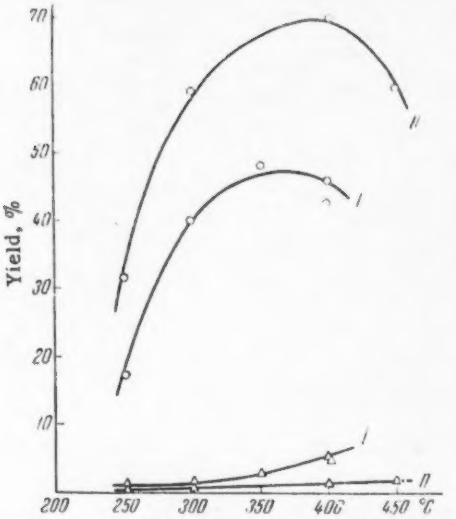


Fig. 1. Effect of temperature on hydrolytic cleavage of mesityl oxide: O) acetone yield; Δ) acetic acid yield. I and II) catalyst samples.

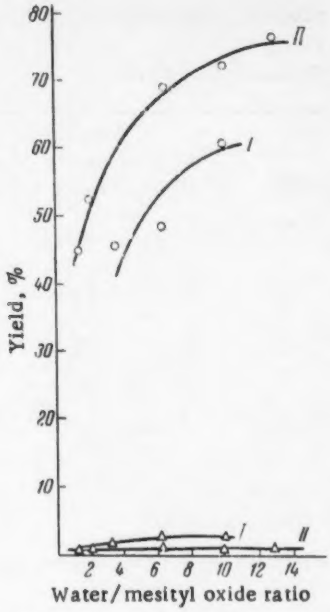


Fig. 2. Effect of relative amount of water on the hydrolytic cleavage of mesityl oxide: O) acetone yield; Δ) acetic acid yield.

TABLE 1

Effect of Temperature on Hydrolytic Cleavage of Mesityl Oxide
Space velocity of passage of mesityl oxide: 0.25 hour^{-1}; contact time 9.5 sec; molar ratio of water : mesityl oxide: 6.3 : 1

No. of expt.	Catalyst sample	Temperature in °C	Yield of react. prod., % of theoretical		Unreacted mesityl oxide, %
			acetone	acetic acid	
1	I	250	17	1,0	73
2	I	300	32	1,2	53
3	I	300	40	0,9	50
4	I	350	48	3,0	44
5	I	400	42	5,2	—
6	I	400	46	4,1	—
7	II	250	32	1,3	61
8	II	300	59	0,6	31
9	II	400	70	2,0	—
10	II	450	60	2,1	—

reaction products were collected in a receiver that was cooled with ice. Gas formation was negligible. Ten ml of mesityl oxide and a known amount of water were passed through in each experiment. Mesityl oxide that was used in the experiments had the following constants: b. p. 129-130° (750 mm), $n^{20}D$ 1.4445.

The reaction products were distilled through a column with 15-theoretical-plate efficiency. Acetone

TABLE 2

Effect of Molar Proportion of Water : Mesityl Oxide in Hydrolytic Cleavage of Mesityl Oxide

Contact time: 10 sec.

No. of expt.	Catalyst sample	Molar ratio of water : : mesityl oxide	Temperature in °C	Space velocity of passage of mesityl oxide in hour^{-1}	Yield of reaction products, % of theoretical		Unreacted mesityl oxide in %
					acetone	acetic acid	
1	I	3,3 : 1	350	0,48	46	1,6	45
2	I	6,3 ; 1	350	0,25	48	3,0	44
3	I	9,9 : 1	350	0,16	61	—	28
4	II	1,3 : 1	400	0,78	45	1,2	—
5	II	2,0 : 1	400	0,78	52	1,3	34
6	II	6,3 : 1	400	0,25	70	2,0	—
7	II	9,9 : 1	400	0,16	72	1,2	24
8	II	12,7 : 1	400	0,12	77	1,4	15

TABLE 3

Effect of Contact Time on Hydrolytic Cleavage of Mesityl Oxide

Temperature 400°, catalyst II

No. of expt.	Molar ratio of water : : mesityl oxide	Space velocity of passage of mesityl oxide in hour^{-1}	Contact time in sec	Yield of reaction prod. in % of theoretical		Unreacted mesityl oxide, in %
				acetone	acetic acid	
1	22,4 : 1	0,78	1,0	30	1,6	—
2	12,7 : 1	0,78	1,7	45	1,5	—
3	6,3 : 1	0,78	3,2	56	1,2	37
4	9,9 : 1	0,16	9,7	72	1,2	24
5	12,7 : 1	0,12	10,7	77	1,4	15

was present in the first fraction with b. p. up to 80° (the main bulk of acetone distilled at 55-57°); this was determined by the oxime method in the presence of methyl orange. The unreacted mesityl oxide (second fraction) distilled at 91.5° in the form of an azeotrope with water, which contained 65% of mesityl oxide [5]. The amount of mesityl oxide was calculated from the weight of the azeotrope that was collected. We ran some preliminary experiments on the analysis of artificial mixtures of water, acetone and mesityl oxide. It was shown that the accuracy of the determination by this method was ±1% for acetone and ±2% for mesityl oxide. The acidic reaction products were determined acidometrically in the presence of phenolphthalein and were recalculated to acetic acid. The products of side-reactions were not examined.

The experiments were run with two catalyst samples: commercial tricalcium phosphate (sample I) and one prepared in the laboratory from calcium chloride and ammonium phosphate (sample II). Both catalysts were dried before use for two hours at 400°. The catalyst was regenerated after each experiment by being blown with air at 450° for two hours. Sample I did not change its activity after 20 hours of work and 10 regenerations. Sample II operated in all over 50 hours and its activity was not decreased noticeably.

The space velocity of passage of mesityl oxide was calculated in liters per liter of catalyst per hour. The contact time (τ) with the catalyst was calculated from the total volume of water vapor and mesityl oxide which passed through the catalyst, using the formula:

$$\tau_{sec} = \frac{V \cdot 3600}{M \cdot 22400},$$

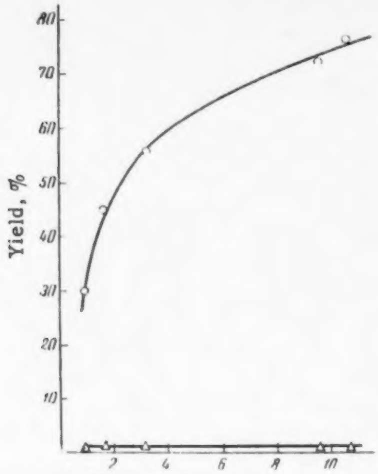


Fig. 3. Effect of contact time on hydrolytic cleavage of mesityl oxide: O) acetone yield; Δ) acetic acid yield.

where V – catalyst volume in milliliters; M/3600 – number of moles of water and mesityl oxide passed over the catalyst per second. The change of the volume of the vapors with alteration of temperature was not used in the calculations.

2. The reaction of hydrolytic cleavage of mesityl oxide was run in the temperature interval of 250-450°. As it is evident from Table 1 and Fig. 1, the degree of conversion of mesityl oxide into acetone increases, with molar ratio of water : mesityl oxide equal to 6.3 : 1 and contact time of 9.5 sec, with elevation of temperature. The yield of acetone over sample II was considerably greater than over sample I under the same conditions. The maximum conversion of mesityl oxide into acetone (48%) was observed at 350° over sample I and at 400° (70%) over sample II. A further elevation of the temperature to 450° or its lowering to 250° led to reduced yields of acetone. The formation of acetic acid was negligible in all experiments. Its maximum yield over sample I was 5.2% at 400° and 2.1% at 450° over sample II.

The effect of the molar ratio of water : mesityl oxide is shown in Table 2 and Fig. 2. The experiments were run under temperature conditions which were optimum for each catalyst sample: for sample I – 350°, and for sample II – at 400°. The contact time was about ten seconds in all experiments. It is evident from Table 2 and Fig. 2 that the degree of conversion of mesityl oxide into acetone over catalyst II rises from 45% to 77% after the increase of molar proportion of water : mesityl oxide from 1.3 : 1 to 12.7 : 1, while the degree of conversion into acetic acid and isobutylene is unchanged. The similar effect of the increased relative amount of water was observed over catalyst I. Conversion into acetone increases greatly with increased contact time from 2 to 4 sec (Table 3, Fig. 3). Then the effect of contact time decreases. The contact time does not significantly affect the conversion of mesityl oxide into acetic acid.

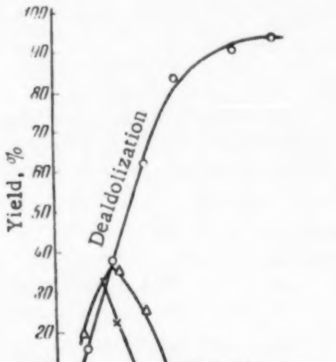


Fig. 4. Effect of temperature on conversion of diacetone alcohol: O) acetone yield; Δ) mesityl oxide yield; x) amount of unreacted diacetone alcohol.

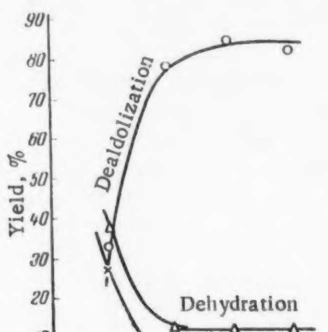


Fig. 5. Effect of temperature on conversion of diacetone alcohol: O) acetone yield; Δ) mesityl oxide yield; x) amount of unreacted diacetone alcohol.

TABLE 4

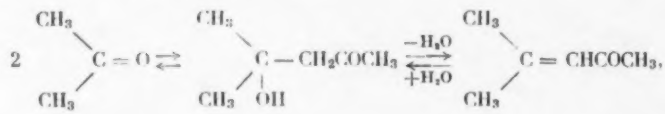
Catalytic Transformations of Diacetone Alcohol Over Catalyst II

Space velocity of passage of diacetone alcohol 0.25 hour^{-1}; contact time 10 sec; molar ratio of water : : diacetone alcohol 6.9 : 1

No. of expt.	Temperature in °C	Yield of react. prod. % of theoretical		Unreacted diacetone alcohol in %
		acetone	mesityl oxide	
1	125	16	19	—
2	150	37	37	21,6
3	175	62	25	6,6
4	200	83	4	2,7
5	250	90	3	0,8
6	300	94	2	0,0
7	150	33	38	27,5
8	200	78	12	3,1
9	250	85	13	0,4
10	300	83	12	0,0

Two experiments were run with liquid phase hydrolytic cleavage of mesityl oxide at elevated temperature and pressure. Catalyst I and a mixture of water and mesityl oxide in molar ratio of 25 : 1 were loaded into an autoclave. The mixture was heated with rotation of the autoclave for one hour at 200°. The yield of acetone was 29.5%. No acidic products were detected. The yield of acetone under the same conditions but without the catalyst was 20.5%. As indicated above, mesityl oxide is not cleaved by running the reaction in the absence of the catalyst in the vapor phase under comparable conditions [7].

3. Since the condensation process is reversible:



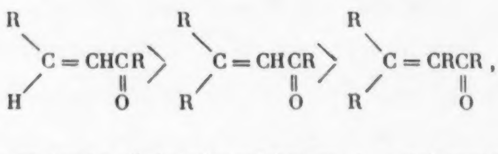
the hydrolytic cleavage of α, β-unsaturated ketones must occur through the same stages of hydration and dealdolization but in reverse order. Actually, it was possible to retard the process at the intermediate stage of hydration with formation of aldols and ketols in the presence of H^+ and OH^- ions [9]. Considering that in our experiments mesityl oxide is converted over calcium phosphate in the same direction as it is in the presence of H^+ and OH^- ions, it was possible to suppose that the reaction proceeds through a hydration stage over the solid catalyst as well. In order to confirm this supposition, we examined the dealdolization reaction of diacetone alcohol over calcium phosphate. The experiments were run in the above-described apparatus of the flow type with 20 ml of catalyst (sample II). The diacetone alcohol had the following constants: b. p. 63-64° (11 mm), $n^{20}D$ 1.4312. The unreacted diacetone alcohol was determined by the oxime method in the presence of methyl orange.

The results of experiments with diacetone alcohol are shown in Table 4 and Figs. 4 and 5. In the group of experiments 1-6 the diacetone alcohol was passed through with water vapor in molar ratio of 1 : 6.9 at space velocity of 0.25 hour^{-1} and with contact time of 10 seconds. It is evident from Table 4 and Fig. 4 that even at 125° (below the boiling point) diacetone alcohol undergoes a transformation in two directions: dehydration into mesityl oxide and dealdolization into acetone. Both processes proceed at about the same rate at temperatures of 125° and 150°. Dealdolization becomes the main reaction at higher temperatures. At 300° the acetone yield reached 94% and that of mesityl oxide was but 2%, no unreacted diacetone alcohol was detected.

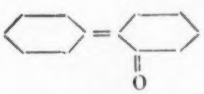
Experiments 7-10 (Table 4, Fig. 5) were run without water feed. The other conditions were the same. Diacetone alcohol underwent approximately the same change in these experiments as it did in experiments with water. The presence of water somewhat lowered the dehydration reaction of diacetone alcohol into mesityl oxide. For example, the acetone yield at 300° was 83% and that of mesityl oxide 12%, while no unreacted diacetone alcohol was detected. No formation of acidic products was observed in all the runs with diacetone alcohol.

We see in comparing the data obtained by us on hydrolytic cleavage of mesityl oxide over calcium phosphate and on diacetone alcohol on the same catalyst, that the dealdolization of diacetone alcohol proceeds more completely and at lower temperatures. Thus, it becomes understandable why diacetone alcohol is not detected among the products of hydrolytic cleavage of mesityl oxide. The absence of acidic products in experiments with diacetone alcohol also confirms the stepwise character of the process. It is natural that very little of acidic products is formed in experiments with diacetone alcohol over calcium phosphate, since acetic acid is the cleavage product of mesityl oxide, and not that of diacetone alcohol. All this permits us to conclude that the hydrolytic cleavage of mesityl oxide over tricalcium phosphate indeed proceeds through a stage of hydration to diacetone alcohol, which is then subjected to dealdolization, while the overall rate of the process is determined by the hydration step.

As indicated by Esafov [10], the overall rate of the process of hydrolytic cleavage of α, β-unsaturated ketones in the presence of H^+ and OH^- ions is limited by the rate of the hydration step, which in turn is limited by the degree of conjugation of unsaturated bonds in the given compound. Since the degree of conjugation decreases in order:

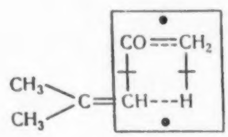


it should be expected that the completely alkylated vinyl ketone: 1-cyclohexylidene-2-cyclohexanone

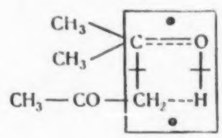


would be more difficultly subject to a hydrolytic cleavage. Data obtained by us, confirm this supposition [11].

Comparing the results obtained with three different solid catalysts: "solid phosphoric acid" type, aluminosilicate and phosphate, we see that the first catalyst almost does not accelerate the reaction of mesityl oxide with water at all, but does cause a cracking of the mesityl oxide molecule with rupture of C−C bond at the α-position relative to the carbonyl group. This transformation may be represented by the doublet scheme:



Conversely, tricalcium phosphate, like the H^+ and OH^- ions, accelerates the hydration reaction of mesityl oxide almost exclusively, with the subsequent dealdolization of the resulting diacetone alcohol. A cleavage of the C−C bond in β-position relative to the carbonyl occurs in this case, following the scheme:



The aluminosilicate catalyst occupies the intermediate position.

SUMMARY

1. Vapor phase conversion of mesityl oxide and diacetone alcohol was studied over tricalcium phosphate.

2. It was shown that like H^+ and OH^- ions, calcium phosphate selectively catalyzes the reaction of vapor phase hydrolytic cleavage of mesityl oxide into acetone.

3. It was found that dealdolization of diacetone alcohol proceeds more completely and under more mild conditions over this catalyst than does the hydrolytic cleavage of mesityl oxide.

4. The results of our work indicate that both in homogeneous catalysis and over a solid catalyst, the hydrolytic cleavage of mesityl oxide proceeds through a hydration step which limits the overall rate of the process.

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BRIEF COMMUNICATIONS

THE RELATIONSHIP BETWEEN ELECTRONIC CHARGES AND LENGTHS OF σ-BONDS

G. V. Bykov

As it was shown previously by this author [1], the shortening of the bond with a π-electronic charge, as compared with the σ-bond taken as a standard, is directly proportional to this charge. It was also shown for C—C bonds that the effect of variations in the σ-electronic charge with the bond length is, relatively, so insignificant that it may be neglected in the calculations. As to the other bonds, this problem still remains unsolved for such bonds to all intents. However in recent years some valuable material was accumulated on the bond lengths at saturated carbon atoms and, although the existing data are at times quite contradictory, it is still possible to make certain generalizations at this time.

1. It was established beyond doubt that with accumulation of halogen atoms, except those of iodine, at the same carbon atom, all bonds of this atom are shortened [2, 3]. This effect has not received a convincing explanation to this day. Therefore, in order not to complicate the study of the interdependence of bond lengths and their electronic σ-charges, such molecules will not be considered further.

2. It was also established that the bonds of carbon with halogens are lengthened under the influence of conjugation with an ethylenic or acetylenic bond. However, these facts have not received any explanation either, unless we consider the trivial concept that the value of the interatomic distance carbon—halogen is determined by the effect of the immediate environment, primarily that of the atoms directly bonded to the given carbon atom [4].

3. As is evident from Tables 1 and 2, such a regularity has a place not only versus C—X bonds (X — halogen) but also versus the C—C and C—H bonds as well. Not only lengthening of bonds relative to the standard bond occurs (the standard being C—C 1.542 A in diamond, C—H 1.093 A in methane) but also shortening: C—C in ethane, C—Cl in cyclopropyl chloride, C—H in three-membered rings. All these facts find an explanation similar to that given for the interatomic distances in unsaturated compounds, specifically: shortening of a σ-bond is greater when its σ-electronic charge is greater and vice versa. Since the charge depends on the atomic electronegativity, that of the atoms which form the given bond and which are directly connected to it, one may judge the bond length by the electronegativity values of such atoms.

Since the electronegativity of an acetylenic carbon is higher than that of an ethylenic carbon, and even still higher than that of saturated one (Table 2), the C—X bonds in propargyl and allyl halides should be longer than those in CH_3X. Here one should expect that the C—Cl bond in propargyl chloride would be longer than the C—Cl bond in allyl chloride, with a refinement of the experimental data. As it follows from the data on the frequencies of cyclopropane [29], bonds C—H in small rings, and hence the C—X bonds as well, have an enhanced σ-electronic charge. This conclusion is excellently confirmed by the example of cyclopropyl chloride (Table 1) and other three-membered rings (Table 2). In ethane, where the σ-electronic charge of the C—C bond A_{CC} = 2.27 e (electron) [27], one should expect some shortening of the C—C bond relative to the standard, while in C_2H_5CN and C_2H_5X one should expect some lengthening, which is confirmed by the data in Table 1.

4. We may suggest the formula:

$$l_{CH} = 1.093 - \Delta^{\sigma}_{CH}(A^{\sigma}_{CH} - 2),$$

TABLE 1

Formula of compound	Bond	Bond length in A*	Formula of compound	Bond	Bond length in A*
$CH \equiv C \cdot CH_2Cl$	C − Cl	1,82 [5]	$CH_2 = CH \cdot CH_3$	C —	2,18 ± 0,03 [4,7]
$CH_3C \cdot C \equiv C \cdot CH_2Cl$	C − Cl	1,82; 1,81 [4] 1,796 ± 0,015 [6]	$CH_3 - CH_2 \cdot CN$	C − C	1,5479 ± 0,0015 [9]
$CH_2 = CH \cdot CH_2Cl$	C − Cl	1,80 [4]; 1,825 ± ± 0,025 [7]	CH_3CH_2Cl	C − C	1,5495 ± 0,0005 [10]
			CH_3CH_2Br	C − C	1,5495 ± 0,0005 [11]
$CH_2 \cdot CH_2 \cdot CHCl$	C − Cl	1,755 [8]	CH_3CH_3	C − C	1,535 [12]
$CH_2 = CH \cdot CH_2Br$	C − Br	1,97 [4]; 2,00 ± ± 0,02 [7]			

*C − Cl in CH_3Cl 1.782, C − Br in CH_3Br 1.938 and C − I in CH_3I 2.140 A [2].

TABLE 2

Formula of compound	C−H bond length in A		Electronegativity of X atom in CH_3X	Electronic charge of C−H bond
	experimental	calculated		
$CH_3C \equiv CH$	1,1124 [13]	—	1,776 [26]	1,8375
CH_3CH_3	1,110 [12]	1,098	1,19 [27]	1,955
CH_3F	1,109±0,010 [2] 1,106±0,001 [14] 1,095±0,010 [15]	1,113—1,122	1,85—2,31 [27]	1,825—1,753
CH_3Cl	1,103±0,010 [2] 1,113 [16]	1,103—1,104	1,39—1,43 [27]	1,911—1,903
CH_3Br	1,101±0,010 [2] 1,113 [16]	1,101—1,103	1,29—1,37 [27]	1,932—1,915
CH_3I	1,100±0,010 [2] 1,113 [16]	1,097—1,100	1,15—1,24 [27]	1,964—1,943
CH_3OH	1,096±0,010 [17,18] 1,098 [19]	1,109—1,117	1,62—2,03 [27]	1,866—1,797
CH_3SH	1,104±0,002 [20,21] 1,091±0,01 [22]	1,098—1,101	1,19—1,30 [27]	1,955—1,930
CH_3SiH_3	1,093±0,005 [23]	1,088—1,090	0,83—0,9 [28]	2,044—2,026
$CH_2CH_2CH_2$	$<$ 1,093 [24]	1,081	—	2,1 [29]
CH_2NDCH_2	1,083 [25]	—	—	2,085
CH_2OCH_2	1,082 [2]	—	—	2,094
CH_2SCH_2	1,078 [2]	—	—	2,128
$(CH_3)_2C = C(CH_3)_2$	—	1,101	1,275 [26]	1,934
$(CH_3)_3C - H$	—	1,107	1,19 [27]	1,88 [27]
$(CH_3)_2CH - H$	—	1,104	1,19 [27]	1,91 [27]
CH_3NH_2	—	1,104—1,111	1,40—1,70 [27]	1,909—1,849
CH_3Li	—	1,076—1,072	0,4—0,5 [28]	2,176—2,143

for the expression of the dependence of lengths and σ-electronic charges in C−H bonds, this formula being similar to the one used for the calculation of lengths of bonds C−H from their π-electronic charges. Substituting into this formula the values of A^{σ}_{CH} = 1.8375 e and l_{CH} = 1.112 Å for methylacetylene (Table 2) we find: Δ^{σ}_{CH} = 0.117 Å/e. Using the values of electronic charges of bonds calculated with the electronegativity values [27] or by other means [26, 29] we may calculate with this formula the values of various bond lengths (Table 2). Excellent agreement is found for methyl halides, except the fluorides, since the electronegativity of fluorine is evidently set too high, which fact is also suggested by the calculations of the dipole moments [30]. A like value of l_{CH} = 1.113 [16] for all three halides is dubious and, on the basis of our calculations, it may be completely

discarded. Evidently the electro negativity of oxygen is also set too high. The C—H bond length in ethane is undoubtedly set too high,but it was determined by an insufficiently reliable method. The calculated value of C—H bond length in cyclopropane is in good agreement with its experimental values for other three-membered rings as well. The formula permits a calculation of σ-electronic charges of C—H bonds in such rings. The calculated bond lengths in a number of compounds which have not been determined experimentally as yet are also given in Table 2.

5. It is easy to see that the phenomena of hyperconjugation are explained naturally by the existence of a relationship between σ-electronic charges and, hence the properties, of C—H bonds on one hand, and the electronegativities of the adjoining atoms, on the other hand. One may judge the difficulties which are now being met in the quantum-mechanical explanation of such phenomena by the fact that it is necessary to resort to such an arbitrary operation as a discussion of three hydrogen atoms of a methyl group as one "pseudoatom" — a donor of π-electrons [31].

SUMMARY

A dependence was shown to exist between the electronic charges and the lengths of σ-bonds of a saturated carbon atom, which permitted us to explain and to correct the existing data on interatomic distances.

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*In this paper on p. 829 line 1 from bottom: should read "connected;" in Table 2 in column for "1" on line 4 from top: should read 1.171; in column for A^{π} between lines 12 and 13 from bottom: should read 0.10; on p. 830 line 14 from top: should read 3.5 ± 0.5; lines 26 and 30: should read "into the system" instead of "system;" p. 831 Table 3 last line: read =N—O— and in Note to the table: should read No. 16 in Table 2.

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**On this page in line 6 from bottom instead of A^{π}_{CH} should read $A^{\sigma\pi}_{CH}$.

CONCERNING THE MECHANISM OF CATALYTIC ACTION OF FUSED IRON CATALYSTS IN SYNTHESES FROM CO AND H_2

Iu. B. Kagan, A. N. Bashkirov, Iu. B. Kriukov, S. M. Loktev and N. A. Orlova

It was shown by us earlier [1] that fused iron catalysts for hydrocarbon synthesis from CO and H_2 which are reduced with hydrogen at 1000° do not have any activity directly after the reduction. Only under the working conditions of the synthesis, during the passage of the gas mixture of CO + H_2 does the catalyst gradually acquire a high order of activity (over 18-20 hours). This treatment of the catalyst is assured by the simultaneous occurrence, under the conditions of the hydrocarbon synthesis, of a number of competing reactions between the components of the reaction mixture on one hand and iron and its compounds on the catalyst surface, on the other hand (carbiding of iron and the hydrogenation of the carbides, oxidation of iron by water, and reduction of iron oxides by carbon monoxide, etc.). As a result of the occurrence of such competing reactions, the metallic iron is repeatedly generated from its compounds in the course of the synthesis, and, on the surface of the working catalyst, there is established a certain dynamic equilibrium of surface phases of various chemical compositions. Activation or "breaking-in" of the catalyst is a result of these processes.

However, neither iron itself nor any of its compounds on the surface of the catalyst which had become active are in themselves the carriers of the catalytic activity. Only a combination of the surface phases, formed in the course of the synthesis, is active – iron, its oxides and carbides. Iron and its compounds which exist on the surface of an active catalyst differ noticeably from the iron formed by high temperature reduction of the catalysts, and from compounds based on such iron. This difference in the properties is shown in the more rapid breaking-in of the catalysts, as compared with freshly reduced ones, which after completion of the activation were treated with hydrogen and then were again tested in the synthesis either directly or after a preliminary carbiding.

EXPERIMENTAL

It appeared practical to establish what new physical and chemical properties are acquired by the catalyst in the activation process which occurs during the synthesis. For this purpose we examined two samples of the same catalyst of the composition ($100\ Fe_3O_4 + 6Al_2O_3 + 4.2\ SiO_2 + 1.2\ K_2O$) + 0.5 Cr: 1) a sample directly after reduction at 1000° and 2) a sample which after the reduction was broken-in under the conditions of the synthesis up to a high order of activity and was then treated with hydrogen in order to reduce iron oxides and in order to hydrogenate its carbides. Specific surface areas of both samples were determined and the rates of oxidation of iron contained in them by water were measured, as well as were the rates of reduction by the carbon monoxide, of the iron oxides that were formed in the process. In addition, we measured the rates of decarbonization of both samples by carbon monoxide and the rates of hydrogenation of iron carbides formed in the process. The rates of the listed reactions were evaluated by the depth of the transformations reached after equal time intervals.

It is evident from the tabulated data that the specific surface area of the catalyst increased by about two-fold as the result of the breaking-in under the conditions of synthesis. Simultaneously the rates of all the reactions studied by us increased noticeably. Specifically the rates of reactions of oxidation of iron by water and hydrogenation of its carbides, at initial stages of its course, rose approximately by 3-4 fold. It follows from this that an increase of the reactivity of iron and its compounds, which exist on the catalyst surface, takes place in respect to their reactions with the components of the reaction mixture, this being a result of the activation

TABLE

Change of Properties of Fused Iron Catalyst as a Result of its Breaking-In Under Conditions of Hydrocarbon Synthesis from CO and H_2

Catalyst sample	Specific surface area in g/sq m	Degree of oxidation by water at 320° in %		Degree of carbiding by carbon monoxide at 320° in %		Degree of hydrogenation of carbides at 320° and 5 atm in %		Degree of reduction of iron oxides by carbon monoxide at 310° and 6 atm in %
		During period from beginning of the experiment, in minutes						
		15	60	15	60	60	120	60
Directly after reduction	1.1	0.5	1.0	1.7	5.3	2.4	6.8	27
Treated with hydrogen after completion of breaking-in	2.4	1.3	2.4	3.9	8.9	8.8	17.2	38

observed by us. The enhanced reactivity of these compounds is evidently a necessary condition for the high activity of the catalyst in the hydrocarbon synthesis. This conclusion was confirmed experimentally by data published earlier by some of us. It was shown that the rates of the appropriate reactions rise tens of times, the specific surface increases six-fold and the catalyst displays high activity in the synthesis even at the very beginning stage of testing, if the temperature of the reduction of the fused iron catalyst is lowered from 1000° to 450°. The synthetic activity of catalysts of different compositions is altered,as a rule,in correspondence with the alteration of their reactivity in reactions with water vapor.

Combination of the accumulated experimental data allows us to suppose the presence of a direct dependence between the catalytic synthesis from CO and H_2 and the reactions which proceed between iron and its surface compounds, on one hand, the reaction mixture components, on the other hand, and to express the hypothesis about the conjugated mechanism of catalytic action of the catalysts being studied. The fact that only a certain combination of surface phases is active in the synthesis, these phases being in a state of dynamic equilibrium, means that the catalyst is active only when a number of competing reactions between the substance of the catalyst and the reaction mixture components (i.e., carbon monoxide, hydrogen and the products of their catalytic interaction) takes place simultaneously. The rise of catalyst activity with the growth of the reactivity of its surface phases indicates that the catalyst is more active if a greater number of CO and H_2 molecules are able to react, under the conditions of the synthesis, with the iron and with its surface compounds. The interdependence between the reactions being studied and the catalytic synthesis from CO and H_2 is revealed in these specific regularities.

The substance of this interdependence may be represented thusly. In the presence of a dynamic equilibrium of the surface phases on the surface of a working catalyst there exist extensive, constantly moving interphase boundaries. Under such conditions the probability is high that on the different sides of the appropriate interphase boundaries, in each region of them, molecules of CO and H_2 enter simultaneously into a reaction with the material of the catalyst. In the course of such reactions, the molecules of carbon monoxide and hydrogen evidently acquire some properties which facilitate their interaction. Owing to this, molecules of CO and H_2 are always present at the interphase boundaries on the surface of a working catalyst and these are in a state of special reactivity for the synthesis. In the presence of the necessary geometric correspondence, these molecules, instead of reacting with the appropriate iron compounds, may react among themselves, forming a primary complex which lays the beginning of growth of a carbon chain. The molecules of CO and H_2 which exist in the active state may enter other reactions which take place during the synthesis, besides the direct interaction among themselves. It is natural that the catalyst should be more active if a greater number of CO and H_2 molecules are capable of entering into a reaction with iron and its surface compounds per unit of time under the conditions of hydrocarbon synthesis, which fact agrees with the experimental data.

SUMMARY

1. An increase of reactivity of iron and of its surface compounds occurs as the result of the activation or breaking-in of fused iron catalysts, which had been reduced with hydrogen at 1000°, under the conditions of synthesis of hydrocarbons from CO and H_2, this increased reactivity being shown in their reactions with CO, H_2 and other reaction mixture components.

2. A hypothesis was advanced about the conjugated mechanism of the catalytic action of iron catalysts, according to which the synthesis from CO and H_2 is induced by reactions of carbon monoxide and hydrogen with the iron and its compounds on the surface of a working catalyst.

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X-RAY STRUCTURAL STUDY OF THE POLYESTER OF EICOSANEDIOL AND DECAMETHYLENEDICARBOXYLIC ACID

Iu. V. Mniukh

The purpose of this study consisted of the clarification of those differences which exist in the structure of the "polythene" type with a rhombic subcell (i.e., cell constructed on the basis of the repeated vectors of the methylene groups) after the introduction of substituents into the molecular chain. Models of the polyester molecules and those of polythene are shown in Fig. 1.

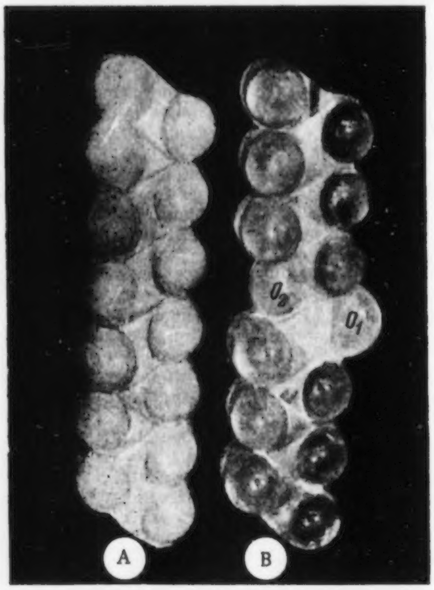

Fig. 1. A. Model of the molecule of polythene. B. model of the molecular chain of linear polyester. The oxygen atom in the C=O group is denoted by O_1. The oxygen atom O_2 "substitutes" for one of the methylene groups.

EXPERIMENTAL

In cases which are similar to the one being considered here and in which the relative number of oxygen atoms in the molecule is not large, the structure retains the subcell which almost coincides in its dimensions with the elementary cell of the rhombic modification of polythene [1]. The following parameters of the subcell were found for the polyester of eicosanediol and decamethylenedicarboxylic acid examined by us: $a_0 = 7{,}407 \pm 0.005$ A; $b_0 = 4.975 \pm 0.005$ A; $c_0 = 2.513 \pm$ $\pm$ 0.005 A.

A calculation of the section $z = \frac{1}{4}$ of electron density (signs of the structural amplitudes were borrowed from paper [1]) showed that the inclination angle of the plane of the zigzag of the molecule relative to b_0 axis is not 41.2°, as found for polythene, but 36°. The reason for this rotation may be understood after an analysis of the dense packing of the molecules of the polyester in the section xy. In the table (also see Fig. 2) we give a comparison of the intermolecular distances in the polyester structure for two cases as follows: hypothetical in which $\varphi_b = 41.2°$, and real, where $\varphi_b = 36°$. It is evident that the angle of 36° is a compromise since its decrease would cause too great a contraction of the intermolecular distance H_1 ——— H_3, while its increase would do the same for the intermolecular distance O_1 ——— H_4.

The isotropic correction for thermal vibrations was introduced in the calculation of the electron density series. The reliability $R = \frac{\Sigma\,(F_{meas} - F_{calcd})}{\Sigma(F_{meas})} = 14\%$, in this case.

Large deviations between the measured and the calculated intensities were found in paper [1] for the structure of polythene and an attempt was made to support these deviations on a theoretical basis by the anisotropy of thermal vibrations and nonsphericity of the electron cloud of the CH_2 groups. We found that the cause of the deviation lies in the lack of allowance for the hydrogen atoms in the calculated intensity values.

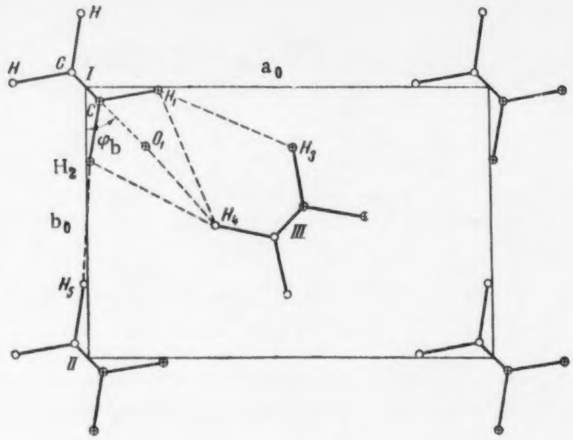

Fig. 2. Rhombic subcell. Axes of the molecules are perpendicular to the plane of the picture.

TABLE

Intermolecular Distances in Structure of Polyester, in A

d_{H---H}	φ_b = 41.2°	φ_b = 36°
H_1 --- H_3	2.48	2.33
H_1 --- H_4	2.92	2.93
H_2 --- H_4	2.86	3.04
H_2 --- H_5	2.43	2.42
O_1 --- H_4	2.26	2.36

The author expresses his gratitude to A. I. Kitaigorodskii for his direction of this work.

SUMMARY

The basic motif of the structure of "polythene" type is retained after the introduction of a small number of ester groups into it. The molecular chains are rotated in this case about the c_0 axis, allowing for a sufficiently good packing of the atoms of oxygen in the C =O groups. An allowance for the hydrogen atoms was shown to be necessary for the calculation of values of intensities of x-ray diffraction in structures of this type.

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LETTERS TO THE EDITOR

REARRANGEMENT OF ALUMINUMTRIALKYLS

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We found, with the examples of triisopropylaluminum and trisec-butylaluminum, that tri-sec-alkylaluminum compounds rearrange on being heated into the tri-n-alkylaluminum compounds:

$$(iso\text{-}C_3H_7)_3Al \rightarrow (n\text{-}C_3H_7)_3Al.$$

The literature method of preparation of tri-isopropylaluminum from di-isopropylmercury and aluminum [1] yields not only tri-isopropylaluminum, as indicated by the authors, but a mixture of tri-isopropylaluminum (b. p. 44-46° (2 mm), m. p. 2° and tripropylaluminum (b. p. 82-84°, 2 mm), does not freeze at −70°), which may be separated by fractionation. The tri-isopropylaluminum prepared by this method is completely converted into tripropylaluminum after being heated in a sealed tube (110-130°, 30 hrs). Tri-isopropylaluminum and tripropylaluminum were identified through the corresponding propylmercuric halides (iso-C_3H_7HgBr, m. p. 95-96°; n-C_3H_7HgBr, m. p. 135°; iso-C_3H_7HgCl, m. p. 94-96°; n-C_3H_7HgCl, m. p. 145°). Tri-sec-butylaluminum, obtained by the reaction of (sec-$C_4H_9)_2Hg$ with aluminum, under the same conditions, rearranges into tri-n-butylaluminum. However, in this case a partial formation of 2-butene and di-n-butylaluminum hydride is observed. Tri-n-butylaluminum was identified through n-butylmercuric bromide, m. p. 136° (sec-C_4H_9HgBr, m. p. 39°).

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ADSORPTION OF TRACE AMOUNTS OF RADIO-ELEMENTS ON NON-ION-EXCHANGE ADSORBENTS

I. E. Starik and I. A. Skul'skii

The rules of the non-ion-exchange adsorption of radio-elements have hardly been studied at all up to the present. A study of these laws is of considerable interest, since the processes of non-ion-exchange absorption of radio-elements play an evidently not lesser role than is played by the ion-exchange adsorption.

We studied the adsorption of Zr^{95}, Nb^{95}, Th^{234}, Pa^{233}, Tl^{204} (I) and Cs^{137} on Ftoroplast-4 (a Soviet variety of Teflon) and on paraffin. The surfaces of these adsorbents are hydrophobic and do not have any ion-exchange

properties. The radio-elements existed in ionic or molecularly dispersed states under the conditions used. The adsorption was studied as a function of concentration of nitric acid and its salts: ammonium and potassium nitrates. It appeared that in the interval from 0.1 N to 3-5 N HNO_3, Zr^{95}, Nb^{95}, Th^{234} and Pa^{233} were adsorbed on Ftoroplast-4 and on paraffin in amounts of 2-6%, from 1 ml of solution, onto 1 sq cm of the adsorbent, while the adsorption of these radio-elements rose by several fold after addition of ammonium nitrate and potassium nitrate. The effect of the salts in this case is analogous to the known effect of salting-out during an extraction with a nonmiscible solvent from an aqueous phase. The adsorption is evidently caused by formation of neutral complexes of the type $[Me(OH)_x(NO_3)_y]^{\circ}$ in the aqueous phase. The adsorption of Zr^{95} and Th^{234} decreases to zero upon increase of nitric acid concentration from 3.5-5 N to 12 N, while the adsorption of Nb^{95} and Pa^{233} is changed insignificantly. This difference in the behavior of the indicated radio-elements may be explained by complex formation of Zr^{95} and Th^{234} with nitric acid. The salting-out effect decreases with increased concentration of nitric acid, the same taking place in the extraction processes.

Analogous dependence on the concentration of nitric acid was observed by a number of investigators in the case of so-called "specific" adsorption of Zr^{95}, Nb^{95}, Th^{234} and Pa^{233} on manganese dioxide, silica, carbon, anion exchange resins and other adsorbents. It is known that these adsorbents are capable of both the ion-exchange and the van der Waals adsorption.

It appears to us, on the basis of these data, that "specific" adsorption may be considered as molecular adsorption. The absence of adsorption of Cs^{137} and Tl^{204} (I) on Ftoroplast-4 and on paraffin, as observed by us, from solutions of nitric acid in the range from 1 N to 12 N and in the presence of salts, may be evidently explained by the strongly basic character of these elements, which do not form any uncharged compounds under the conditions used.

Studies in this direction are continuing.

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ISOMERIZATION OF 2-VINYLBICYCLO-(2,2,1)—5-HEPTENE INTO THE TETRAHYDROINDENE SYSTEM

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Recently we prepared 2-vinylbicyclo-(2,2,1)-5-heptene (I) (b. p. 140.4° (760 mm), $n^{20}D$ 1.4808, d^{20}_4 0.8884; bromine number 243.5; found C 89.92%, H 10.16%) by the diene condensation of cyclopentadiene with butadiene (145°, 3 hours, yield: 19%). In studying its properties we discovered that it undergoes a new type of isomerization (flow system, 300°, yield: 50%, or 150° 88 hours, yield: 46-48%) into the tetrahydroindene system (b. p. 160.3° (760 mm), $n^{20}D$ 1.4978, d^{20}_4 0.9261; bromine number found 255.5, calculated 266.1; found C 89.98%, H 10.13%; calculated for C_9H_{12} C 89.96%, H 10.04%).

It was shown that the isomerizate has the carbon skeleton of tetrahydroindene since after its hydrogenation (Pt, 20°) hydrindane is formed while on dehydrogenation (Pt, 300°) indane is formed. However, since the infrared spectrum of the isomerizate* showed three lines in the region of 700-750 cm^{-1} and four lines in the region of 1600-1660 cm^{-1}, which characterize the vibration of C=C bonds [710(115), 732 (33), 750 (28), 1602 (4.8), 1617.5 (6.6), 1636.5 (8.2) and 1655 (7.8) cm^{-1}] the isomerizate is evidently a mixture of two or three isomers (A, B, C) with a different position of the double bonds.

*The spectral study was done by A. V. Iogansen at the VNIINP.

(I) A B C

This isomerization does not proceed through the stage of a decomposition of I into the original components with a subsequent reaction of cyclopentadiene–dienophile and butadiene–diene, but apparently occurs as the result of a rupture of the C–C bond in the endomethylene bridge and a closing of a new ring at the vinyl group and the carbon of the endomethylene group; a stabilization of the resulting biradical then follows. The presence of the vinyl group is necessary for this isomerization since neither 5-ethylbicyclo-(2,2,1)-2-heptene nor 2-ethylbicyclo-(2,2,1)-heptane undergo such a reaction.

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NOTE ON THE RAMAN SPECTRA OF CERTAIN CYCLOPROPANES

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and Kh. E. Sterin

We succeeded for the first time in separating into stereoisomers the substances 1,2-diphenylcyclopropane and 1-phenyl-2-cyclopropylcyclopropane; their properties are as follows: 1,2-diphenylcyclopropane – cis- form: f. p. 131.6-131.7° (4.8 mm), b. p. 36.7°, $n^{20}D$ 1.5887, d^{20}_4 1.0290; trans-form: b. p. 144.1-144.2° (5.2 mm), f. p. 15.3°, $n^{20}D$ 1.5997, d^{20}_4 1.0346; 1-phenyl-2-cyclopropylcyclopropane: cis form: b. p. 100.2-100.5° (11 mm) $n^{20}D$ 1.5330, d^{20}_4 0.9574; trans-form: b. p. 111.3-111.5° (13.8 mm), $n^{20}D$ 1.5371, d^{20}_4 0.9585.

We examined the Raman spectra of both pairs of stereoisomers and found a sharp increase, relative to alkylbenzenes, of the integral intensities of the characteristic lines of the benzene ($\Delta \nu$ about 1200 and 1600 cm^{-1}), especially clearly shown in the spectra of 1,2-diphenylcyclopropane. This effect speaks of the presence of a considerable conjugation of the phenyl rings with the three-membered ring; it was first shown experimentally by us in the case of phenylcyclopropane [1] and was later discussed in the work of Levina and co-workers [2]. The conjugation effect in the spectra of the lower boiling isomers (see above) is noticeably weaker. This may be explained by steric hindrance, which disturbs the most advantageous disposition of the phenyl rings for conjugation relative to the three-membered ring. A simple calculation shows that such hindrance is possible only for the cis-isomers. In accordance with this we related the stereoisomers in both cases to the cis- and trans-forms, although this does not agree with the Auwers-Skita rule. A more detailed current study will be published later.

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CHRONICLE

Nikolai Nikolaevich Kachalov

(On 75th Birthday)

The Corresponding Member of the Academy of Sciences USSR, Laureate of the Stalin Prize, Professor Nikolai Nikolaevich Kachalov began his work activity in 1902 as an operator in Ural iron mines, and later worked as an assistant to the manager of a coal mine shaft in Donbass near Iuzovka (Stalino). After completion of studies at the Mines Institute in 1911, N. N. Kachalov entered the Peterburg Porcelain Factory (now M. V. Lomonosov Factory) where he passed from a laboratory assistant to the Technical Director of the plant. During the period of 1911-1916 Nikolai Nikolaevich developed at that plant the technology of preparation of soft porcelain, and organized the production of new highly artistic articles and arranged for the production of industrial porcelain, at that time a completely new operation.

The necessity for organization of production of optical glass in Russia appeared during the First World War. In August of 1914 N. N. Kachalov began some experiments searching for the methods of its preparation. In this period, N. N. Kachalov, jointly with N. S. Kurnakov, D. S. Rozhdestvenskii, V. E. Tishchenko, V. E. Grum-Grzhimailo and I. V. Grebenshchikov, developed the technology of production of optical glass, using the experience of old foreign European factories. Toward the end of 1916, the first Russian factory for optical glass was constructed, but soon thereafter was made inoperative during the period of the foreign military intervention and civil war, and was restored only in 1923. From 1923 to 1930 N. N. Kachalov occupied the post of the Technical Director of the optical glass plant. During this period an original, considerably more progressive technology of production of optical glass was developed at this plant and the Soviet land obtained the possibility of being completely free of imports of optical glass. During the same period the production of a number of other forms of industrial glass was developed at the same plant.

Along with studies in the field of optical and industrial glass, N. N. Kachalov continued his work in the field of ceramics as well. In 1918 the State Ceramic Research Institute (Leningrad) was created with direct participation by N. N. Kachalov; the latter worked at this institute until 1930 as the Deputy Director and President of the Scientific Collegium. The groups of collaborators of this institute (G.I.K.I.) and of Lenzos conducted, under N. N. Kachalov's direction, an extended study of the technology of production of fireclay materials used in glass-making, and studied in detail the properties of native high-quality clays. The results obtained from these studies were summarized in the publication of "Fireclay-Masses" which constituted a considerable contribution to the science of the silicates.

Since 1930 N. N. Kachalov has been a Professor of the Leningrad Technological Institute of Lensovet, where he organized the Chair on Glass. During a period of some years, N. N. Kachalov combined the work of this Chair with work at the State Optical Institute as a Deputy Director in connection with industry and later as the builder and director of an experimental plant. N. N. Kachalov widely developed a number of scientific studies at the Lensovet Leningrad Technological Institute. The personnel of the Chair on Glass conducted important studies under his direction, which laid the foundation for modern production of colored glass, developed the recipes for artistic enamels, studied the properties of a number of glasses, developed the recipes for chemically resistant glasses for laboratory ware and for acid resistant enamels. Since 1935 N. N. Kachalov and his co-workers have been conducting extended systematic studies of the processes of polishing and grinding of glass. Shortly before the Great National War* N. N. Kachalov began his work on production of sculptures and architecturally artistic articles of glass, in a creative partnership with the National Artist of USSR V. I. Mukhina, and organized the production of these articles at the Leningrad Mirror Factory, now reorganized as the Factory for Artistic Glass.

*World War II.

In 1948 the Institute of Silicate Chemistry of the Academy of Sciences USSR was organized at the initiative of Academician I. V. Grebenshchikov, and in the organization of this institute the most active part was played by N. N. Kachalov who, in addition, headed the laboratory of cold treatment of friable materials in this Institute. The work by N. N. Kachalov in the field of grinding and polishing of glass provided the scientific foundation for the production of polished sheet glass and was very important for planning new establishments of this nature. N. N. Kachalov gave the most serious scientific aid to our native glass-making by his various studies.

A remarkable pedagogue, lecturer and scientist, N. N. Kachalov is the author of many publications. His fundamental works "Basis for Production of Optical Glass" and "Basis for Processes of Grinding and Polishing of Glass" have an outstanding significance. At the peak of a remarkable career, N. N. Kachalov completed a large item of work with two major books "Glass" and "Textbook of Technology of Grinding and Polishing of Sheet Glass."

N. N. Kachalov combines the scientific and the pedagogic activity with a considerable amount of social work: since 1934 until the present he has been often elected as regional or municipal representative, and since 1953 — Leningrad Area Soviet of Workers' representative. N. N. Kachalov is a member of many scientific councils of research institutes and technical councils of plants. For his contributions to the development of native glass industry and for his scientific work, N. N. Kachalov was awarded the name of Distinguished Scientific and Technical Worker and that of the Laureate of the Stalin Prize. N. N. Kachalov was awarded the Order of Lenin, two Orders of Red Labor Banner, Order of the Red Star and also some medals.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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